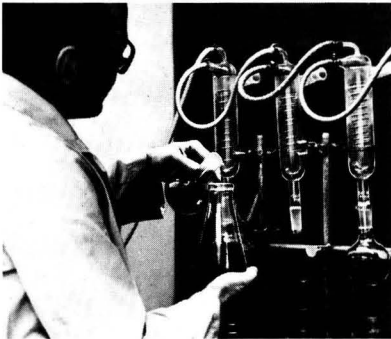# ES&T

**BIOMASS
CONVERSION**
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This issue contains no papers for which there is supplementary material in microform.

DEPARTMENTS

MacDonald's farm today

Old MacDonald still has his farm and his herd of ferthings. These animals, it may be recalled, are susceptible to a fatal water-borne disease called *hyfertitus*.[a] Two decades ago, on the basis of an economic model, MacDonald installed a water treatment unit called a "Disinfeclarminator" to destroy the pathogens that caused *hyfertitus*. The results were more groats (profit) for MacDonald, practical experience in statistics and epidemiology for his daughter, Honoria, and a sale for Young Sam, the equipment salesman. Furthermore, the model for ferthings was applied to people by Honoria's professor to provide a rationale for the setting of all criteria, standards, or rules for administration of man's environment. Among the professor's several conclusions was the observation that "The setting of any quality criterion or standard relating to health and well-being inevitably entails making an implicit estimate of a cost:benefit ratio based on whatever data or other factors are available for judgment." The professor's results were well received by academics in ivory towers and also by some engineers in practice, but were largely ignored by public decision makers.

Events have occurred that are causing MacDonald to reexamine the technology used for a conventional Disinfeclarminator in water treatment. A powerful oxidant, oozine, is used to destroy the pathogens. This chemical also reacts with naturally occurring organic substances found in all water sources to form polyoozopanes (POPs), substances that may exert toxic effects on ferthings. Furthermore, like all water and wastewater treatment systems, each Disinfeclarminator unit produces a waste requiring disposal. The question "To treat or not to treat?" answered succinctly by the economic model, has been replaced by "Where to dump?" The question is clear but the answer is not.

Federal legislation has restricted the discharge of pollutants into surface waters and the atmosphere and also encouraged the land disposal of wastes. The purposes of this legislation are laudable, and many of the results are beneficial to humankind and to the environment. Other returns are of less value or even detrimental. In MacDonald's case, substances formerly discharged to the environment are being stockpiled, awaiting disposal. "Zero discharge" to surface waters can merely mean relocation to another site.

New knowledge has changed both the costs and the benefits in MacDonald's economic analysis. It is true, as stated by Honoria's professor, that "To set a criterion is to impute a cost–benefit ratio." It is also true that developments in science and technology change this cost–benefit ratio. The changes may be favorable or unfavorable. A consequence of these changes is that rules require reevaluation.

The control of environmental quality involves complex social, legal, political, economic, scientific, and technological issues. For some time administrative solutions have been promulgated with insufficient regard for the advice of Honoria's professor and for scientific and technological understanding. What is MacDonald to do about the POPs in his water and the wastes from his treatment plant? What is society to do with its pollutants? As we reevaluate our rules, let us use science, technology, and economics more extensively and more advantageously than in the past. The alternatives are expensive and ineffective.

[a] Thomas, Harold A., Jr. *The Quarterly Journal of Economics* **1963**, *LXXII*, 143–48, reprinted in *Journal of the American Water Works Association* **1964**, *56*, 1087–91.

Charles R. O'Melia

ES&T
LETTERS

Educational opportunities

Dear Sir: The Harvard School of Public Health is seeking candidates for enrollment in its graduate programs in occupational and environmental health. People qualified for enrollment range from recent bachelor's degree recipients to mid-career professionals. Areas in which enrollees can specialize include air pollution control, occupational health, industrial hygiene, radiation protection, and environmental health management. Supplementing the teaching program are extensive opportunities for research, both for MS and doctoral candidates, in the development and application of techniques for monitoring worker and public exposures to airborne particulates and gases, the development of mathematical models for estimating exposures in indoor and outdoor environments, air and gas cleaning including the control of naturally occurring airborne radionuclides in buildings, the application of physical and chemical methods for identifying the sources of specific environmental contaminants, and the evaluation of associated risks. A range of traineeship and fellowship support is available. The deadline for applying for fall 1983 admission is March 1, 1983. Potential applicants should contact the Department of Environmental Health Sciences, Harvard School of Public Health, 665 Huntington Ave., Boston, Mass. 02115; (617) 732-1169.

Dade Moeller, chairman
Dept. of Environmental Health Sciences
Harvard School of Public Health
Boston, Mass. 02115

Drinking water disinfectants

Dear Sir: I read with interest the feature article on drinking water disinfectants in the October issue. (*ES&T*, Vol. 16, No. 10, p. 554A) Last year this time I was a Fulbright-Hays Senior Lecturer in Liberia, West Africa. Before drinking the water there it had to be filtered, boiled 20 minutes, and refiltered.

One of the true pleasures in returning to the U.S. is being able to drink water from the tap.

I ask your readers to keep the water problem in perspective. The major public health problem the world faces is supplying its developing population with "safe" drinking water. Most of these people face a lifetime of chronic "runny belly." While we in the U.S. are concerned with mutagenic effects of disinfectant by-products in order to prolong our life to an excess of 70 years, the remaining three-fourths of the world is plagued by contaminated water.

Let us not neglect these people with the greatest need.

Robert J. Hargrove
Associate Professor of Chemistry
Mercer University
Macon, Ga. 31207

Dear Sir: In the October 1982 *ES&T* feature article "Health effects of drinking water disinfectants and disinfectant by-products" by R. J. Bull, several facts pertinent to the evaluation of drinking water disinfectants have been omitted. Bull cites several animal studies (*1, 2*) in a discussion of chlorite and its role in methemoglobinema and hemolytic anemia. Bull failed to report, however, that in a recent study human adult males were given drinking water with various levels of chlorine dioxide, chlorite, chlorate, chloramine and chlorine (*3, 4*). Quoting from that report, "In general, the study affirmed the relative safety and tolerance of normal, healthy adult males and normal, healthy adult male G-6-PD deficient individuals to daily twelve week ingestion of 500 mL of chlorine disinfectants at a concentration of 5 mg/L." This report was sponsored by the U.S. EPA Health Effects Research Laboratory, project officer R. J. Bull.

In a recent epidemiologic study also conducted by U.S. EPA Health Effects Research Laboratory (*5*), 198 persons were exposed for 3 months to drinking water disinfected with chlorine dioxide. Bull does cite this report but does not mention the finding that this "study failed to identify any adverse effects associated with a twelve week exposure to chlorine dioxide disinfected drinking water."

Finally, in Bull's discussion of the carcinogenic and mutagenic activity of a disinfected water supply, he states, "Previous work has shown that treating Ohio River water with either chlorine, ozone or chloramine increased the numbers of tumors in SENCAR mice . . ." What Bull fails to mention is that in the same experiment Ohio River water treated with chlorine dioxide and dosed to the SENCAR mice in the same manner as the other disinfectants did not produce tumors in the test animals (*6*).

I agree with Bull's opinion that it is ". . . too early to provide any definitive answer to the question of the relative health risks of the various drinking water disinfectants." But excluding pertinent experimental and epidemiological data from a review article will not expedite the process of assessing the health effects of drinking water disinfectants.

Marco Aieta
143-B Escondido Village
Stanford, Calif.

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(2) Abdel-Rahman, M. S.; Couri, D.; Bull, R. J. *J. Environ. Pathol. Toxicol.* **1980**, *3*, 431.
(3) Bianchine, J. R.; Lubbers, J. R.; Chauhan, S.; Miller, J.; Bull, R. J. "Study of chlorine dioxide and its metabolites in man," EPA-600/1-81-068, NTIS PB82-109356.
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(6) Bull, R. J. *J. Am. Water Works Assoc.* **1980**, *72*, 245.

Author's response

Dear Sir: In some respects Marco Aieta's comments concerning my article in the October issue of *ES&T* are justified. However, I would like to point out that this paper was essentially a reprinting of the paper I presented at Asilomar at the 4th Conference on Water Chlorination. Dr. Joseph Bianchine reported on the human studies at the same conference.

Therefore, I felt it inappropriate to present Dr. Bianchine's data in my paper. This explains the lack of reference to the human studies in the *ES&T* article.

It should be noted, however, that the conclusion quoted by Aieta does not rule out an effect in humans. The 5 mg/L dose used in the clinical study was one-tenth of that required to see effects in experimental animals. The epidemiological study quoted was conducted after ClO_2 disinfection had ceased for a short period of time. Consequently, conclusions of neither study contradict animal studies if that is Aieta's concern. The major question, however, is not what ClO_2 and its by-products do to normal humans, but what they do to people who are very sensitive to hemolytic agents. Neither the clinical nor the epidemiological studies adequately addressed this issue.

I have more difficulty with Aieta's charge concerning the SENCAR data. The data from that experiment are included in the article quoted in *ES&T* with the results of two additional studies of the same design. On balance there is nothing to indicate a consistent

difference between the disinfectants with experiments of this type. Consequently, to take the standard suggested by Aieta is indefensible in view of present information. These data are in press in *Environmental Health Perspective* (reference #41) and will be available soon.

Richard J. Bull, director
Toxicology and Microbiology Division
Health Effects Research Laboratory
U.S. EPA
Cincinnati, Ohio 45268

Crop losses and air pollution

Dear Sir: Bette Hileman's recent article (*ES&T*, Vol. 16, No. 9, p. 495A) describing crop losses caused by air pollutants and the research under way to assess losses was excellent. I wish to comment and elaborate on some items in the article.

There is increasing evidence that ozone damage to crops is widespread in the eastern half of the U.S. as well as in Southern California. Frequently ozone injury to leaves is ignored because it is thought to be natural leaf senescence, which is somewhat similar in appearance. With ozone injury the older leaves became chloratic, or yellow prematurely, have a wide range of leaf markings primarily on the upper leaf surface, and leaves may drop from the plant. Ozone causes destruction of chlorophyll; consequently, photosynthesis declines. If more persons could see, as I have, at mid- and late season the dark-green, old as well as young, leaves protected against ozone-induced leaf injuries in the open-top chambers supplied with charcoal-filtered air (e.g., potato leaf, p. 498A) and the yield increases of crops such as soybeans, cotton, potatoes, tomatoes, sweet corn, snap beans, lima beans, etc., they would be more interested in the problem. The open-top chambers used in the National Crop Loss Assessment Network (NCLAN) permit the culture of many crops from the seedling stage to maturity with minimal chamber effects.

Interest in surface ozone (as contrasted to stratospheric) measurements and in crop losses due to ozone air pollution was stimulated about 25 years ago by the discovery that elevated ozone levels caused injury to leaves of grapes in California and tobacco in the eastern U.S. (Richards, B. L.; Middleton, J. T.; Hewitt, W. B. *Agronomy J.* **1958**, *50*, 559; Heggestad, H. E.; Middleton, J. T. *Science* **1959**, *129*, 208). At that time the primary concern, especially regarding tobacco, was the injury to leaves. In the past decade, we have learned that yield

reductions due to ozone in ambient air can be significant for ozone-sensitive crop species and cultivars. Sometimes this occurs with very little visible injury to leaves. Also, there may be leaf injuries without significant loss in yield of seed or fruit.

A major deficiency in making regional or national estimates of crop losses is the inadequacy of ozone monitoring data for agricultural areas. I find it difficult to believe that some countries in North Carolina appear to have higher ozone levels than other locations in the U.S. (map, page 497A, September 1981 *ES&T*). However, an average 7-h ozone level of 0.07–0.08 ppm, indicated for North Carolina, was found by EPA at 27 of 171 U.S. sites included in an analysis of mean 2-month values in 1975, 1976, and 1977. Twenty-one sites had 2-month average 7-h levels of ozone ranging from 0.08 to 0.11 ppm, and for Philadelphia and Los Angeles the ozone levels were higher (EPA. "Evaluation of alternative secondary ozone air quality standards"; OAQPS 78-8, IV-A3, U.S. E.P.A.: Research Triangle Park, N.C., 1979). Most of the sites were identified as urban centers; a few were rural.

Analyses of data sets for 1979 and subsequent years and additional monitoring in rural areas, including those that may have only normal background levels of ozone, are needed. There should be more monitoring and data analyses also at the NCLAN sites so the ozone exposure doses received by the plants in the chambers, now measured and controlled with the probes in the chamber centers near the top of the plant canopy, can be better related to ozone in ambient air some distance away from the crop and the chambers and at 3 m (height of sampling for SAROAD monitors). NCLAN participants follow an established general protocol, but each year the scientists from different disciplines meet to review results, set priorities, and modify plans to improve efficiency and the data base. During the year, NCLAN's very dedicated Research Management Committee handles many matters by conference calls. I strongly support a statement made in your article that the data generated by the program ". . . are absolutely necessary for making meaningful cost–benefit analyses . . ."

Howard E. Heggestad
Research Plant Pathologist
U.S. Department of Agriculture
Agriculture Research Service
Beltsville, Md. 20705
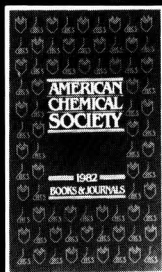
ES&T
CURRENTS

The West German Minister of the Interior Friedrich Zimmermann has signed draft proposals to reduce SO_2 emissions by 50% from large furnaces that burn fossil fuels (including utilities). The proposals have been submitted to interested parties for comment. At the June 1982 Stockholm Conference on Acidification of the Environment, the Social Democratic government announced that it would reduce emissions by this amount. Since then, however, the government changed hands, and it was not known whether the new government would follow this policy. Concern that acid deposition and SO_2 may be damaging West German forests is one of the primary reasons for these proposals.

New evidence that pollution from coal-burning and factories in the Midwest is the major cause of acid rain is provided by an extensive study prepared for EPA by 46 industry, government, and university scientists. The 1200-page report is in draft stage and is subject to further review by the government. It says that natural causes of acid rain are "insignificant" and that timber and mining operations have not caused the acidity found in a large number of lakes. The report also notes that "growth reductions are occurring" in many forested areas where the rainfall is highly acidic but asserts that there is no conclusive proof that acid rain retards forest growth.

The Justice Department has formally cited executive privilege in backing EPA administrator Anne M. Gorsuch's refusal to produce thousands of documents Congress has requested. Rep. Elliott H. Levitas (D-Ga.) had subpoenaed Gor-

such to appear before the House Public Works and Transportation Investigations subcommittee with all documents concerning the 160 toxic waste sites listed for cleanup under Superfund. Documents on three of the sites had also been subpoenaed by Rep. John D. Dingell (D.-Mich.), chairman of the Energy and Commerce oversight subcommittee. The subcommittees

Gorsuch: refuses to supply documents

argue that they need the documents to determine whether Superfund is being adequately administered. Gorsuch says that the documents would disclose EPA's methods of forcing parties responsible for waste sites to clean them up.

A suit to halt the startup of a dormant nuclear reactor at the U.S. Department of Energy's (DOE's) Savannah River plant in South Carolina has been filed by a group of environmental organizations. The suit seeks to force DOE to halt renovation on the reactor, which makes materials for nuclear weapons, until DOE prepares a detailed environmental impact study. According to a less-detailed DOE assessment, radioactive wastes, containing 46 curies of radioactive cesium, will be flushed into the Savannah River by cooling water if the reactor resumes operations. Georgia Gov. George Busbee says

that 40–50 times the normal amount of radioactive tritium has already been found in milk and water in Georgia, and he is opposing any expansion of the Savannah River plant.

Eighty percent of the funds for a large acid deposition research project have been cut by the Office of Research and Development at EPA, following a directive received from the Office of Management and Budget (OMB). The project, called the Advanced Utility Simulation Model (AUSM) development project, was entering its third year when OMB suddenly directed that no more than $150 000 should be allocated to it. The planned funding level was $650 000, down from the $821 000 spent in 1982. The AUSM was to have provided an analysis tool for determining the cost to the utility industry of proposed acid rain control strategies and the resultant changes in emissions that would result. The model is thought essential for assessing the overall effectiveness of proposed acid rain control measures.

A new device called the Webster–Heise valve may substantially reduce automotive tail-pipe emissions, increase fuel economy, and make it possible for vehicles to run on low-octane gasoline, according to a report issued by the Congressional Research Service. The device is a variable atomizing valve that is installed on the intake manifold below the carburetor. It contains two mesh screens that vaporize the gasoline rapidly, thus causing more rapid combustion. So far the auto industry has been skeptical about the valve, but the Department of Transportation has started testing the device extensively.

Risk estimates provided by quantitative risk assessment are highly unreliable but are given undue

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weight in regulatory actions, according to EPA draft staff papers. The documents said that lifetime risk estimates of cancer are a function not only of the method but of the accuracy of the input data, and "unquantifiable uncertainties" are involved in both of these factors. Therefore, the practice of using quantitative risk assessment to rank different pollutants for regulatory action is highly questionable. Furthermore, the prospects for improving the estimates or for placing bounds on the inherent uncertainties are problematical, the papers said.

EPA's fiscal 1983 budget includes $49 million more than the Reagan administration requested for state grants. The approved amount, $231.1 million, is still about 4.5% less than the $236 million provided for state grants in 1982. EPA administrator Anne M. Gorsuch said at a meeting of representatives of the National Governors' Association that she wants to eliminate state grants eventually. Spokesmen for the governors' association say that state grants are critically important and that it is unrealistic to think the states can continue to run environmental programs without federal funding.

Three large nuclear power plants have been cancelled recently. Duke Power Company stopped construction on two reactors near Gaffney, S.C., on which $68 million had been spent since work began in 1974. A Duke spokesman said the plants were cancelled because of a declining growth in the demand for electricity. In addition, the Virginia Electric and Power Company ceased construction on the North Anna Unit 3. The company is requesting a rate increase to cover the $540 million that has already been spent on the plant. A sharp increase in estimated construction costs, from $2.2 billion in the late 1970s to $5.1 billion, caused the reactor to be cancelled.

Comprehensive new standards to protect Florida's groundwater from contamination were adopted by the state recently. With these new regulations, Florida is taking the lead in protecting groundwaters, according to scientists at the Depart-

ment of Environmental Regulation. The new rules expand the definition of groundwater to include two classifications; apply secondary drinking water standards to Florida's aquifers; add minimum water quality criteria; create more restrictive zones of discharge; and encourage recycling of wastewaters. Discharges to drinking water aquifers must fulfill both primary and secondary drinking water criteria.

Several western governors are asking that a number of federal rules for coal leasing be withdrawn. They argue that the new regulations diminish the states' power to control the development of coal reserves. In general, the governors want to develop coal more slowly than Interior Secretary James G. Watt intends. Current new regulations allow the Interior Department to ignore the recommendations of regional groups. The governors claim that excessive leasing will result in a reduction in mineral leasing revenues because the present coal market is poor.

A $38.5 million settlement to clean up four toxic waste sites in St. Louis, Mich., was reached between EPA and the Velsicol Chemical Company. The sites contain polybrominated biphenyls (PBBs) and tris, which was used as a flame retardant for children's pajamas. PBBs made by Velsicol were accidentally mixed with feed several years ago and killed thousands of cattle. According to the settlement, all the hazardous wastes will be buried in "impermeable" clay at the company's plant site, and the company will be required to monitor the site for 30 years. Some environmentalists doubt that the landfill solution will be adequate because they believe that landfills generally are ineffective in the long run.

The Harrison Prescott Eddy Medal of the Water Pollution Control Federation for 1982 went to Peter Nelson and Anne Chung of Oregon State University, and Mary Hudson, now a sanitary engineer at Yellowstone National Park. They were recognized for their paper, "Factors Affecting the Fate of Heavy Metals in the Activated Sludge Process." They explained

an equilibrium chemical model incorporating conditional adsorption constants and the model to predict the distribution of metals between soluble chemical species and "surface complexes."

Nelson: shared Eddy medal

Groundwater's chemical composition should be included as a nuclear waste disposal site selection criterion, Jess Cleveland of the U.S. Geological Survey suggested to the American Chemical Society. Such composition might have a significant effect on the rate of leaching of plutonium from borosilicate glass and on the solubility of the plutonium in water. Tests on four different groundwaters showed plutonium solubility highest in basalt groundwater and lowest in shale groundwater. Fluoride in basalt water and sulfate in shale water may have some effect, but Cleveland feels that groundwater make-up is site-specific.

Breast cancer might be linked to a fossil fuel combustion by-product, warn Jack Bartley and Martha Stampfer of the Lawrence Berkeley Laboratory. This byproduct, benzo[a]pyrene (BaP), was transferred to a special culture of human mammary epithelial cells—the type involved in 80–90% of breast cancers and 99% of breast tumors. Apparently, the cells readily metabolized the BaP to a BaP diol epoxide which, in turn, reacted with and modified the cell DNA. The scientists found that the BaP metabolic effect may be exacerbated by other factors, such as dietary fat, especially polyunsaturated fat.

Some fog water may contain enough dissolved chemicals to corrode metal, damage vegetation,

and, perhaps, menace human health, say scientists at the California Institute of Technology. They measured fog pH and chemical composition at three sites in Los Angeles and Bakersfield, Calif., but noted that the same phenomenon could be found elsewhere in the U.S. and abroad. The scientists found pHs of 2.2–4.0, as well as nitrates and sulfates, ammonia, copper, iron, lead, nickel, manganese, and organic compounds. Concentrations of up to 12 000 μeq/L of nitrate and 5000 μeq/L of sulfate were observed.

The first solid-state electrolyte analyzer to measure SO$_2$ in flue gas directly within the flue has been introduced by Westinghouse Electric Corporation. The company says that the analyzer can be used in flue gases with temperatures as high as 1400 °F. The sensing cell's output voltage is logarithmic with SO$_2$ content of flue gas. The device can read levels as low as ppm or as high as percentage quantities for sulfur burner applications. Since the system operates in conjunction with an in-situ oxygen analyzer, SO$_2$ values are found by subtracting oxygen values from total measurement values.

Methanol as fuel: Will it work as a practical bus diesel substitute? What about emissions? Acurex Corporation (Mountain View, Calif.) will learn the answers to these questions for the California Energy Commission under a 2½-year, nearly $2 million program. Methanol-fueled buses will run from Marin County to San Francisco and back for one year. Careful analyses will be made of fuel consumption, emissions, performance, and durability. It is hoped that methanol, which can be made from coal, can help cut oil import needs and also reduce bus emissions, since there would be no diesel particles and less NO$_x$ if things work as expected.

New and emerging technologies for hazardous waste control were the subject of an effort initiated by EPA (Cincinnati, Ohio) and contracted to Ebon Research Systems (Washington, D.C.). The need for a data base or a newsletter for these technologies was evaluated. Among technologies examined were molten salt combustion, high-energy electron treatment, chemical dehalogenation, and ultraviolet (UV) light with hydrogen or chlorinolysis. While advantages and disadvantages of each must be weighed carefully, these technologies should be considered as alternatives to landfills, according to the study.

Solar collector array

Solar heating and cooling on a large scale will be tested at Georgia Power's corporate headquarters building in downtown Atlanta. The system is expected to furnish 30% of the heating and cooling requirements of the 24-story building. There are 1482 parabolic trough collectors to provide heat to water flowing into a heat exchanger. Heated water gives power to an absorption chiller for cooling purposes. The chiller's excess heat will be used for water and space heating. The system is computer-controlled to provide what the users feel will be the optimum mix of solar and conventional energy sources.

INDUSTRY

To control pollution, the chemical industry is expected to have spent as much as $970 million in 1982. That figure represents 6.31% of the $15.38 billion spent for new plants and equipment. In 1981, pollution control spending was believed to be $800 million, or 6.47% of the $13.6 billion new plant and equipment outlay; 1980 figures were $730 million for pollution control or 5.9% of the $12.6 billion new plant and equipment outlay. These figures were furnished by the Bureau of Economic Analysis of the U.S. Department of Commerce.

Electricity from the biggest U.S. "wind farm" may be sold to Pacific Gas & Electric (PG&E) by 1985. The plan is to install 36 Boeing generators, each of which would be rated at about 3500 kW; expected project cost is $400 million. The project builder and operator would be AeroTurbine Energy Corporation (Denver, Colo.). The planned site is the point where the Sacramento and San Joaquin Rivers enter San Pablo and San Francisco bays. Generation starts with 14-mph winds and is most efficient with winds at or above 27.5 mph. Windmill shutdown occurs at wind speeds of 60 mph or more.

A data base for the prediction of biological activity will be distributed by Comtex Scientific Corporation (New York, N.Y.). The data base uses molecular structural activity relationships to predict, for instance, bioaccumulation, biodegradability, and toxicity, according to principles set forth by Corwin Hansch of Pomona College (*ES&T*, Vol. 15, No. 4, p. 381). Presently, 28 parameters are listed for over 2800 substituents, and partition coefficients are given for more than 22 000 solutes. The data base has already been used for ethical drugs and various pesticides and is planned as a tool for quantitative prediction of bioactivity.

EPA's decision to ban toxaphene use will not be contested by the marketer of the chemical. "Although we disagree with EPA conclusions, we do not intend to challenge the cancellation because of the extreme cost associated with legal proceedings," said BFC Chemicals, Inc. (Wilmington, Del.). BFC asserts that EPA "has made it clear that their hazard evaluation is based on 'worst-case' analysis," and that "many assumptions of an extreme nature, some of which are contrary to known facts, have been used in the risk assessment." The company says that widely publicized residues in Great Lakes fish may not be toxaphene, as the EPA document acknowledges, and that no illness showed up in employees even after 30 years of manufacture, equaling about 1000 man-years of exposure.

ES&T's 1983
Advisory Board
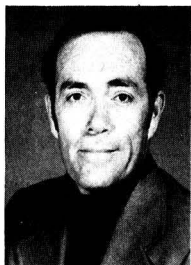
Dr. Russell F. Christman, editor, has announced the appointment of two new members to the *ES&T* advisory board. **Dr. Lawrence H. Keith** is a chemistry development coordinator at Radian Corporation in Austin, Tex. His research interests include analysis of organic compounds in environmental samples, the development of new analytical methods for trace level analysis of organics, and safe handling of hazardous materials. **Dr. Eugene B. Welch,** professor of applied biology in civil engineering at the University of Washington in Seattle, has served as program director for environmental engineering and science since 1980. He has been most active in the research area of eutrophication, nutrient cycling, and lake restoration and is also interested in the ecological effects of wastewater. A third member of the board, **Dr. Julian B. Andelman,** was reappointed to another term.

Board members serve three-year terms. The last year of each member's term is noted in parentheses.

The PCB imbroglio

*Airing the health effects of polychlorinated biphenyls
is a good place to begin unraveling the confusion*

Polychlorinated biphenyls (PCBs) are a family of 209 chlorinated aromatic hydrocarbons. About 100 of these PCBs are used commercially. The public now knows that PCBs are persistent in the environment and is concerned that they may have harmful health effects. These chemicals can accumulate in the food chain; this accumulation is related to their relative insolubility in water and their high solubility in lipids, such as body fats. Called bioconcentration, this action causes tissue levels of PCBs to be elevated to levels orders of magnitude higher than aqueous concentrations of these chemicals.

In the U.S., the control of PCBs was mandated by Congress under the Toxic Substances Control Act (TSCA) of 1976. PCBs were the only chemicals singled out for specific attention by this law. Because of their stability, PCBs biodegrade very slowly, and they are widespread in the environment.

Since the enactment of TSCA, considerable scientific data concerning their human health effects have become available. Although the recent literature is voluminous, the information indicates that no substantial adverse human health effects have resulted from exposure to PCBs in the U.S. Some people are beginning to say that had this information been available in 1976, PCBs might not have received special treatment in the law. They point out that the hue and cry of the Yusho experience put pressure on the Congress to do something. That something is the TSCA.

But regulations issued under this law have not made the problem go away. Between 1929 and 1977, about 1.2 billion lbs of PCBs were produced
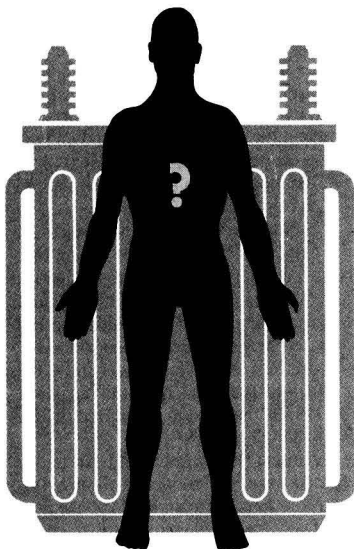
in the U.S. Although U.S. chemical manufacture of PCBs has now ceased, an estimated 750 million lbs are still in use. PCBs are used in two major types of electrical equipment—in transformers that raise or lower the voltage of a power line and in capacitors, those bread-box-sized cans on utility poles that help maintain constant voltage in homes. PCBs are also present in other types of electrical equipment including electromagnets and voltage regulators in fluorescent lighting fixtures. According to one EPA estimate, there are 20 million lbs of PCBs in storage.

Over the years, careless disposal of PCBs has contaminated the surface of soil and aquatic systems in the U.S. But the situation is not unique to this country. The OECD (Organisation for Economic Cooperation and Development) in its publication *The OECD Observer* (September) noted that despite the fact that production and use

of PCBs decreased dramatically in accordance with a 1973 OECD decision, disposal facilities are still needed to prevent environmental contamination by these chemicals.

The regulation trail

TSCA was passed in 1976; in 1977, the manufacture, processing, distribution, and use of PCBs (in a non-totally enclosed manner) were banned. But in May 1979, the EPA promulgated a rule establishing exceptions to the general ban. One of the 1979 exceptions permitted the use of PCBs in certain electrical equipment. EPA classified the "use" of this equipment in a "totally enclosed manner," in effect allowing this type of use to continue. Another exception established what has become known as the 50-ppm cutoff point. EPA determined that PCBs in concentrations below 50 ppm were not covered by the TSCA Section 6 (e) ban. Hence, oils and other items containing less than 50 ppm PCBs are not covered by the regulation.

Then, in 1980, in considering a suit filed by the Environmental Defense Fund, the U.S. Court of Appeals for the District of Columbia Circuit set aside these two exceptions to the ban and required the agency to look at the situation again. The court said, in essence, that the use of PCBs in some of the equipment is not in a totally enclosed manner and there is no justification for setting the 50-ppm regulatory cutoff for PCBs levels.

A first part of the EPA response to the court was due on August 1982; it dealt with the use of PCBs in electrical equipment. A second part, which was due in October 1982, partially dealt with the issue of 50 ppm. Further rule making is under way to complete

EPA's response to the remand of the 50-ppm cutoff. The 50-ppm level was stayed by the court to allow EPA time to complete its rule-making activities. Hence, EPA anticipates that the cutoff will be in effect for another two years, while EPA completes its rule making.

In response to the first part of the court order, EPA authorized the use of PCBs in certain types of electrical equipment, set forth conditions for the continued use of PCBs, and established schedules for phasing out certain PCBs transformers and capacitors. This final rule making required inspections and record keeping, among other requirements, and was immediately challenged by a host of organizations, including the Edison Electric Institute, the National Rural Electrical Cooperatives Association, the Environmental Defense Fund, the Natural Resources Defense Council, and the American Frozen Food Association. A further pronouncement from the Court of Appeals for the D.C. Circuit is imminent.

Addressing the information needs of the electric utility managers, Executive Enterprises, Inc. (New York), sponsored a meeting in Washington, D.C., at which the recent EPA regulations that are being challenged anew were discussed. The meeting on Oct. 15 addressed such questions as: What does the law say that you can or cannot do with PCBs legally? What are the problems and requirements for record keeping? What, if any, enforcement actions may the EPA be taking? In brief, there were sessions on the regulations affecting the use of PCBs, spill cleanup and reporting requirements, practical problems in complying with PCB regulations, and PCB enforcement.

Health effects meeting

An open discussion on the health effects of PCBs was initiated this May. Sponsored by the EPA, on short notice to the public, a two-day symposium for scientific information exchange on PCBs was conducted under contract with ICAIR (Cleveland, Ohio). One objective of the meeting was to review, discuss, and interpret scientific data on PCBs published since 1978 and preliminary PCB data from ongoing work. Another objective was to identify research gaps and areas of agreement and controversy. Proceedings of the May 12-13, 1982, meeting in suburban Washington, D.C. (Bethesda, Md.), entitled "Recent Advances in Exposure, Health, and Environmental Effects Studies on PCBs," are

expected to be available in June 1983. Meanwhile, tapes of sessions of the symposium are available from Bowers Reporting Company (Falls Church, Va.).

Yusho, a unique experience

The Yusho (rice oil) poisoning occurred in 1968. The Yusho experience was described at an international workshop in Washington, D.C., held on March 17-19, 1980. In the proceedings of the workshop, "Plans for Clinical and Epidemiological Follow-up after Area-Wide Contamination," Robert W. Miller of the National Cancer Institute (NCI) said that the Yusho disease was first recognized because of an epidemic of chloracne that began in February 1968 on the island of Kyushu, Japan. One thousand fifty-seven people were affected; their illnesses—chloracne, headaches, nausea, and diarrhea—were quickly traced to a heat-transfer agent used during the manufacture of cooking oil. The oil contained 2000-3000 ppm PCBs, now known to be contaminated with impurities.

Some scientists and physicians in Japan and Taiwan are now saying that the Yusho effects are due to high levels of other contaminants in the rice oil, such as chlorinated dibenzofurans and quaterphenyls, which are considerably more toxic in animal tests than PCBs. The average level of total ingestion of PCBs has been estimated to be 0.5-2.0 g.

Among the 11 children born to exposed women, two were stillborn and three others were small-for-date. All showed transient symptoms such as dark cola-colored pigmentation and eye discharges. These observations indicate placental transfer of the agent. Infants who were breast-fed had higher serum PCB levels. A 13-year follow-up (1981) found PCBs in the tissues of breast-fed children, the level varying with the duration of breastfeeding. (Scientists are asking how these levels differ from the background level in the general population.) Follow-up of the affected population, thus far, has not revealed carcinogenesis or other clear evidence of adverse health effects related to this experience.

In the follow-up of some of the chloracne cases at Kyushu University there are some reports that second pregnancies, one year or more after the mothers' exposure to PCBs, seem to result in darker-than-usual (hypermelanotic) infants. Chloracne in patients first seen in 1968 persisted for two or three years.

This experience in Japan focused

attention on PCBs problems elsewhere in the world. In the U.S., Holly Farms, Inc., a supplier of chickens and eggs, discovered reduced hatchability of its eggs, and traced the problem to PCBs contamination of chicken feed. No human exposure was reported in this case, which occurred in 1971. The contamination occurred in a manner similar to that of the Japanese cooking oil. PCBs, containing impurities and used as a heat-transfer fluid, leaked into the feed through pinhole erosions in the pipes.

In 1980, a second chloracne epidemic, involving 1000 persons, developed in Taiwan. Again, the source was traced to cooking oil contaminated with PCBs during manufacture. This is very similar to the Yusho experience, according to a Japanese publication on the subject.

In summary, the combination of PCBs with chlorinated dibenzofurans and quaterphenyls has caused area-wide food contamination. These chemicals may have a transplacental effect, produce chloracne, and be transmitted in breast milk.

Occupational experience

Workers in the electrical industry have been exposed to PCBs since the materials were first introduced around 1930. Aside from infrequent skin conditions which disappeared when exposure to PCBs was discontinued, no significant adverse health effects have been reported. The absence of significant health effects, even among workers with higher exposures to PCBs than Yusho patients has been explained by the absence of chlorinated dibenzofurans in the commercial mixtures.

Irving Selikoff of Mt. Sinai School of Medicine (New York) said very extensive studies on PCBs have been done. A study of workers in the largest capacitor plants in the U.S., at Fort Edward and Hudson Falls, N.Y., was published in the *Annals of the New York Academy of Science* in 1979. Some skin effects were observed but no serious disease was reported.

In another study that has been under way for more than three years, Selikoff is investigating employee mortality in these capacitor plants. Under the direction of William J. Nicholson of Mt. Sinai, this study is jointly supported by the National Institute for Occupational Safety and Health (NIOSH), the United Electrical Workers Union, and the American Cancer Society. Selikoff indicated that a report on this study would be available in the spring of 1983.

Structural similarity of toxic compounds[a]

Overlay of planar conformation of 3,3′,4,4′,5,5′-hexachlorobiphenyl with TCDD[b]
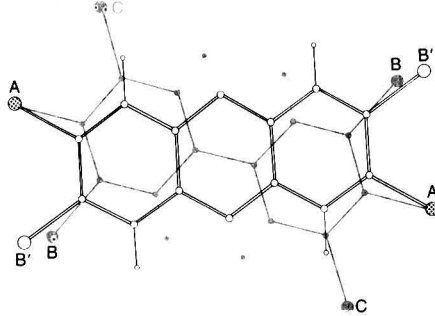
[a]Toxic structures show preferred distribution polarization about the lateral chlorine atoms (A, B, and B′) through resonance interactions between rings. (Atoms C are also chlorine but are not in a lateral position.)
[b]TCDD   2,3,7,8-tetrachlorodibenzo-p-dioxin

Correlation of biological activity of individual PCB compounds in animals with molar polarizability

The critical rectangular distances in the molecule (3 × 10 Å) between lateral chlorine atoms appear in the most toxic structures . . .

Name of compound	Single oral dose in guinea pig LD$_{50}$ (μg/kg)	Type of inducer of mixed-function oxidase activity in rat	Pm (molar polarizability)
2,3,7,8-tetrachlorodibenzo-p-dioxin	2	P-448	—
2,3,7,8-tetrachlorodibenzofuran	7	P-448	—
3,3′,4,4′,5,5′-hexachlorobiphenyl	500	P-448	106
3,3′,4,4′-tetrachlorobiphenyl	< 1000	P-448	110
. . . whereas deviation from the rectangular arrangement significantly lowers the biological potency			
2,3,7-trichloro-p-dioxin	> 29 000	—	—
2,3,3′,4,4′,5,5′-heptachlorobiphenyl	> 3000	P-450, P-448	116
2,2′,4,4′,5,5′-hexachlorobiphenyl	> 10 000	P-450	157

Source: James McKinney, NIEHS

Selikoff indicated that researchers have measured the levels of PCBs in serum and in fats; currently, they are investigating dibenzofurans. This investigation is under the direction of Mary Wolff, head of the analytical chemistry unit of the environmental sciences laboratory of Mt. Sinai.

Last year, David Brown of NIOSH (Cincinnati, Ohio) reported a mortality study of 2500 PCBs-exposed electrical equipment workers from two capacitor manufacturing plants. More than 50% of these workers were exposed to PCBs on the job for more than 20 years; some were exposed for as long as 40 years. The results showed no significant excess in total mortality from cancer, cardiovascular disease, neurological manifestations, or any other cause. The overall mortality was low; overall cancer death was lower than that of the general population. If PCBs are carcinogenic, they are weak agents in humans.

In another study, Alexander Blair Smith also of NIOSH looked at workers from a capacitor plant and two electrical utility plants that loaded transformers with PCBs. His conclusion, published in 1981, was that although there were high levels of PCBs in the blood, "none of the published occupational and epidemiological studies (including our own) have shown that occupational exposure to PCBs is associated with an adverse health outcome, except for the occurrence of chloracne during the early years of its manufacture and use, and possibly during current times as well, depending on circumstances of its use and exposure."

In November 1982, NIOSH initiated a new research project to learn the reproductive history of women exposed to PCBs in the workplace. Under the direction of Michael Rosenberg, the study will look at 800 women who worked in a capacitor plant. A sample of 200 married women who worked directly with PCBs will be compared to a matched group of 200 women whose exposure was low or in-

cidental. A questionnaire covering demographic data, occupational history, and medical history will be completed for each of the 400 workers.

Toxicological study

In August 1981, a consulting firm specializing in toxicology was charged with examining the toxicological and epidemiological literature on PCBs. The firm was to provide a professional opinion on the implication of these studies for the human health effects of PCBs. The study was performed by Drill, Friess, Hays, Loomis, and Shaffer, Inc. (DFHLS—Arlington, Va.) and was sponsored by the Electric Edison Institute and the National Electrical Manufacturers Association (NEMA). This study was undertaken in response to the previously mentioned court order.

DFHLS reported that it is not apparent how the Yusho experience—exposure by ingestion—can be related to exposure to PCBs in the U.S. workplace. Although total PCBs ab-

sorbed were similar for both groups, the dose patterns were different. The U.S. industrial worker had essentially a low-level, long-time exposure to PCBs by inhalation and skin contact. In contrast, the Yusho experience was by ingestion over a short period of time. Because of the predominant role of impurities such as chlorinated dibenzofurans in the rice oil, the study concluded that it is not possible to extrapolate acute and subchronic effects of commercial PCBs mixtures on humans from the Yusho experience.

Of the various effects noted in animal test systems, the DFHLS study found that only dermatological effects, including some chloracne and an increase in liver enzyme activity, have been clearly demonstrated in human populations at the dosage levels associated with occupational exposure. It is the firm's opinion that the risk to human health from even high level occupational exposures has been shown by the studies available to be low; therefore much lower human exposures to PCBs in the workplace and in the natural environment do not present significant human health risks.

In response

Irwin Baumel, director of the Health and Environmental Review Division of the U.S. EPA, commented on the DFHLS study. In an April 12, 1982 internal memo to Martin Halper, director of the EPA, he wrote, ". . . this document is very well prepared and knowledgeably written; however, it presents a review of selected reports. . . . This document contends that the studies reviewed demonstrate that PCBs do not pose any serious risk of injury to human health. While we have completed only a preliminary review of this document, we do not agree that the information presented proves that PCBs do not pose any serious risks. Specifically, the areas of hepatotoxicity, mutagenesis and reproductive effects are of greatest concern and must be fully investigated."

In rebuttal to the EPA criticism, Seymour L. Friess, president of DFHLS, cautioned that "it should be emphasized that such differences in interpretation can well arise among scientists from consideration of experimental and observational studies that are not perfect or complete in every report, and that may be contradicted in other reports."

He continued, "To say that the literature on PCBs is voluminous would be an understatement of the first magnitude. DFHLS considered only those papers which, in their judgment, made a meaningful contribution to a determination of potential health effects in the human."

The view of the Chemical Manufacturers Association (CMA) is: "Any exposure to PCBs does not pose a significant health risk to humans." The CMA paper, "Summary of Health Effects of PCBs," dated November 1981, was prepared by Ecology and Environment, Inc. (Buffalo, N.Y.).

The science

Under a section in its report entitled "other health effects—enzyme induction," the DFHLS study says that the predominant effect of commercial PCBs shows up in the tests involving cytochrome containing monooxygenases, which are a family of enzymes involved in the metabolism of various toxicants.

In recent scientific research, James McKinney of the NIEHS (National Institute of Environmental Health Sciences, Research Triangle Park, N.C.) assessed the structural requirements that are important for the toxic properties of halogenated aromatic hydrocarbons. He and colleagues investigated the specific structural requirements for induction of cytochrome P-448, cytochrome P-450, and associated monooxygenase activities in rats and mice, and toxicity in the guinea pig. The guinea pig appears to be an extremely sensitive animal model for the toxic effects of these compounds. It is now quite clear that molecular geometry and electronic properties are important in eliciting biological activity of this type.

McKinney and E. McConnell in a recent publication said that studies of structural specificity for the receptor with model compounds, including several PCBs, has led them to postulate that polarizability properties are an underlying electronic basis for this activity. Measurement of this molar polarizability (Pm) for a selected number of PCBs has indeed shown a clear correlation between this property and the ability to induce cytochrome P-448, cytochrome P-450, or to be a noninducer.

All four P-448 inducers tested in this study had a Pm value of 113 ± 7, with the two mixed inducers at the high end of the range. The four strong P-450 inducers had a Pm value of 153 ± 9. The noninducer tested had a very high Pm of 211. How to calculate molar polarizability is explained in a short communication in *Chem. Biol. Interact.*, **1981**, *34*, 373–78.

With the P-450 data there is no correlation between activity in rat and guinea pig toxicity data for PCBs. On the other hand, there is a correlation between P-448 activity and toxicity data in the guinea pig. McKinney says, however, "We don't know what this correlation means." He adds that there are species differences. The important question now is determining whether or not the so-called mixed inducers, (those compounds that show both P-448 and P-450 activities) are toxic.

At present, the mechanism by which P-450-inducing PCBs operates is unknown. P-448 inducers, however, are thought to interact with a specific cytoplasmic receptor, presumably a protein. Ability to bind effectively to this receptor is postulated to involve a particular spatial relationship of electronegative groups, which is dependent upon the ability to achieve a degree of coplanarity of the two phenyl rings.

With dibenzodioxins, dibenzofurans, and naphthalenes, for example, coplanarity is built into the molecular structure. In the case of PCBs, revolution around the biphenyl linkage allows the molecules to seek their lowest energy conformation. McKinney and Phirtu Singh found that for the two pure P-448 inducers, the preferred crystallographic structures are significantly nonplanar, but non-ortho substituted biphenyls can be cocrystallized in a coplanar state. As orthochlorines are added, the tendency for coplanarity decreases and is precluded by two ortho-chlorine atoms. Similarly, as ortho-chlorine atoms are added, McKinney's data indicate that enzyme induction tends to shift from P-448, to mixed or noninducing, to P-450.

The pure P-448 inducers, 3,3′,-4,4′-tetra and the 3,3′,4,4′,5,5′-hexachlorobiphenyls, are present in commercial mixtures in the low ppb quantities, if at all—too low to have biological significance. Therefore, the major relevance of McKinney's work on exposure to commercial PCB mixtures must be in the study of mixed-type and P-450 inducers. As shown in the table, these are considerably less toxic than the pure P-448 inducers

Prognosis

It now seems clear that new insights are being found to explain the toxicity of cytochrome P-448-inducing chemicals. More work needs to be done to understand the implication of these insights to human and environmental exposures to PCBs.

—Stanton Miller

1982 Stockholm Conference on Acidification of the Environment

*Through a glass selectively—or some governments
saw what they wanted to see*

A new, and somewhat unexpected, international development concerning acid rain occurred last year. For the first time, a major industrial nation—a major polluter—joined the Scandinavian side in its views about the seriousness of the acidification problem. Until recently, West Germany vigorously defended the idea that not enough was known about the problem to warrant control actions. Now the West German government has adopted a diametrically opposite view and announced a new policy of reducing SO_2 emissions by 50%. Switzerland also has changed its position and allied itself with those countries who favor near-term emission control at pollution sources.

What persuaded these two countries to abandon their previous positions were disturbing revelations linking acid deposition, including the dry deposition of SO_2, to "crown dieback" in forests over widespread areas of West Germany and to the almost complete destruction of large stands of trees in the neighboring high-altitude forests of Eastern Europe.

This information was revealed and discussed intensively at the 1982 Stockholm Conference on Acidification of the Environment. The conference consisted of three related international meetings. The first two were expert meetings attended by scientists—one on ecological effects of acid deposition and the other on strategies and methods to control emissions of sulfur and nitrogen oxides. The third was a ministerial conference of government representatives.

The attendees included over 100 scientists and nearly as many representatives from 21 countries, five international organizations, and observers from many nongovernmental organizations. The countries repre-

Since 1965, nearly half the spruces have died on Camel's Hump in Vermont's Green Mountains. Mounting evidence suggests that acid rain may be the cause.

sented were among the 34 signatories to the Convention on Long-Range Transboundary Air Pollution, an international agreement negotiated in 1979 by the United Nations Economic Commission for Europe (ECE).

Before the Stockholm meeting began, many participants expected it to reveal little that was new and to emphasize what had been emphasized at previous meetings—namely, the very widespread acidification of lakes in Scandinavia. Instead, the conference focused on a different problem—more complete evidence strongly suggesting that ambient sulfur dioxide

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Selected conclusions from the experts' meeting

• "The main acidifying atmospheric pollutants are SO_2 and NO_x." Within the industrialized region "man-made sulfur emissions exceed the natural emissions by a factor of five to twenty."

• "Nitrate ions made available from atmospheric deposition play a minor role in water acidification today except during winter and early spring 'acid surges.' "

• "Ammonia emissions also influence acidification. In Europe and North America domestic animals and fertilizers are thought to be its main sources with emissions comparable to those of NO_x."

• "The atmospheric lifetime of $\frac{1}{2}$ to 2 days for dry deposited SO_2 corresponds to a mean transport distance of a few hundred km. Sulfate is removed primarily by wet deposition and has a lifetime of 3–5 days. This corresponds to a mean transport distance of the order of a thousand km."

• "If a general decrease in emissions were to take place within a large industrialized region (of the order of a thousand km), specific areas within this region might experience significantly smaller or larger decreases in deposition. However, the total deposition over the whole industrialized

region would decrease approximately in proportion to the reduction in emissions."

• "Future acidification and reversal of present acidification of surface waters in sensitive areas receiving high sulfur deposition would be reduced by a decrease in the present level of sulfur deposition."

• "Any reduction in acid deposition must be beneficial to aquatic ecosystems under acid stress."

• "Empirical data from Sweden, Norway, Canada, and the U.S. show that lakes in sensitive areas, with alkalinity ≤ 50 μq/L have in general not been acidified when the catchments receive a sulfur load of 0.5 gS/m²·y or less."

• "In sensitive areas with deposition >0.5 gS/m²·y, many surface waters have been acidified."

• "In Ontario, Canada, about 50 000 lakes on granitic terrain receive ≥ 0.7 gS/m²·y, and 2500 lakes surveyed in the area indicate that 20% have alkalinity <40 μeq/L. In Quebec the extent of sensitive lakes is even greater. Based on the Scandinavian experience, these lakes are expected to undergo acidification in the next several decades."

• "Acidic groundwaters (some-

times with pH <4.5) have been reported from some countries in Europe. In acid groundwater, concentrations of Al, Cu, Zn, and Cd are often 10–100 times higher than in neutral groundwater."

• "There is evidence to suggest that tree growth may be decreased in association with annual mean concentrations as small as 25–50 μg SO_2/m^3. These concentrations prevail over large parts of Europe." [The primary standard for SO_2 in the U.S. (annual arithmetic mean) is 80 μg/m³. This level is found regionally throughout the upper Ohio River basin and locally elsewhere in the eastern U.S.]

• "There is concern that large amounts of acidic deposition, occurring in some areas, may be decreasing the ratio of calcium:aluminum in soil solutions to an extent that impairs root growth and endangers tree survival."

• "The recently reported forest damage in an estimated one million hectares of Central Europe seems to be related to (among others) the direct effects of gaseous pollutants and soil impoverishment, and toxicity arising from very large amounts of wet and dry deposition."

and acid deposition may be damaging trees in West Germany and other parts of Central Europe. The experts' meetings produced a consensus report that paid a great deal of attention to this research and summarized it as follows: "The recently reported forest damage in an estimated one million hectares of Central Europe seems to be related to (among others) the direct effects of gaseous pollutants and soil impoverishment, and toxicity arising from very large amounts of wet and dry deposition."

This conclusion was drawn largely from the work of several West German scientists, but especially Professor Bernard Ulrich of Göttingen University, who has been studying the effects of air pollutants on forests since 1966. In the paper he presented at the first experts' meeting, he offered the rather startling conclusion that, "No forest ecosystem, even forests on calcareous soils, can withstand the present [West German] air pollution without serious damage," and that "in the long run, trees will not get older than 30 to 40 or

50 years, even under optimal soil conditions."

Soil chemistry changes

It has been known for many years that sulfur dioxide gas at high peak ambient concentrations causes direct damage to vegetation. What is new in Ulrich's and other related research is that the continuing deposition of comparatively low concentrations of SO_2 and acid rain can cause indirect effects on forests, by gradually changing the soil chemistry over many years.

According to Ulrich's work, forest damage occurs in four stages. In the first stage, trees benefit from the increased sulfur and nitrogen content in the rain and grow faster than they would without it. This stage is the one that has been most often observed in short-term studies.

During the second stage, as the result of ion exchange and leaching progressing downward through the soil, the soil's neutralizing capacity is impaired by the cumulative effects of

many years of continuing sulfur and acid deposition. The soil loses much of its ability to supply nutrients such as calcium and magnesium that are essential for tree growth.

The third stage is a period of destabilization. At this time, continuing deposition of sulfuric acid and SO_2 mobilizes aluminum and heavy metals from the soil. Aluminum is present in most soils, but in an insoluble form. Acid deposition releases the aluminum, making it available in soil water to damage the fine root hairs with which trees absorb nutrients and water from the soil. During this stage, the Ca/Al ratio in the soil solution and in the roots becomes less than unity. Dissolved aluminum becomes toxic and, at Ca/Al ratios below 0.15, causes complete growth inhibition.

At this point the ecosystem has lost its resilience and is likely to enter the fourth or succession stage. To push a tree over the boundary between apparent health and impending death, all that is required is one or more added stresses that may be a normal part of

its life cycle, such as a succession of warm, dry years. In cool, wet years, dissolved organic matter in the soil may chelate the Al and prevent aluminum toxicity. When the soil remains dry over a period of time, however, there is an increase in internal soil acidification and a decrease in dissolved organic matter. Then, according to Ulrich, "higher concentrations of unchelated trivalent Al ions will appear in the soil solution and cause heavy root dieback." This may lead to the death of the tree. Because death often occurs in a period that is drier than normal, the tree may appear to die from drought, when in fact drought may be merely the triggering factor that releases a chain of events brought about by the acidification of the ecosystem.

On sensitive soils, tree death from dry deposited SO_2, acid rain, and other acidifying processes takes many years because the soil behaves like an ion exchange column. At first only the upper layer is affected. Gradually, continued acid deposition affects successive soil layers until it changes the chemical makeup of the layers where the root hairs are located.

Ulrich also pointed out that the destabilization period, the third stage, makes the tree susceptible to many other stresses such as disease and insect attack on the leaves. Root-decomposing fungi, stimulated by acid stress, can damage woody roots and make the tree vulnerable to being blown down in heavy windstorms.

Ulrich's theories are highly controversial. Some scientists have expressed doubts that forests on calcareous soils in the U.S. are subject to damage from acid deposition.

Bolstering positions

At the experts' meeting, those in attendance, over 100 research scientists, produced a consensus report that contains some rather strong conclusions, not only about forests, but about several other aspects of acid deposition (see box, p. 16A). For the ministerial conference that followed, the representatives of some governments searched the experts' report for statements supporting their own governments' positions. Countries determined to control emissions found many statements pointing to the need for urgent emissions reductions—especially decreases in SO_2. These nations include the Nordic countries, Canada, Switzerland, The Netherlands, Belgium, Austria, and West Germany. Indeed, the U.S. and Great Britain were the only two countries that spoke

out strongly against immediate reductions and demanded that more research be performed before any controls are considered.

The speech of Kathleen Bennett, EPA assistant administrator for air, noise, and radiation, chose very small portions of the experts' report and, from these, created an argument that appeared to bolster the U.S. position. In addition, she repeatedly emphasized that emissions of SO_2 and other pollutants are declining in the U.S.

As evidence of uncertainties associated with acid deposition, she quoted the following statement from the experts' report: "If a general decrease in emissions were to take place within a large industrialized region (of the order of a thousand km), specific areas within this region might experience significantly smaller or larger decreases in deposition." But she omitted the sentence following this, which states that "the total deposition over the whole industrialized region would decrease approximately in proportion to the reduction in emissions."

As further evidence of great uncertainty and a reason for not decreasing emissions at the present time, Bennett emphasized her concern that a deposition threshold for harm to aquatic systems had not been identified at the experts' meeting. She insisted that a threshold for protecting terrestrial and aquatic ecosystems from harm does exist and postulated that this "threshold" lies somewhere between 0.5 and 1.5 gS/m^2·y. She also said that "many waters have been acidified" in regions where the sulfur loading is

1.5–3.0 g/m^2·y. It is known that wet sulfur deposition alone in some sensitive parts of the northeastern U.S. is now at a level of ~1.6 g/m^2·y, and if dry deposition is added to this, the total is about double that in many regions. Therefore, some sensitive areas of the U.S. are now receiving enough sulfur to harm aquatic life, and the relevant finding in the experts' report appears to be that "any reduction in acid deposition must be beneficial to aquatic ecosystems under stress."

In her speech, Bennett stated repeatedly that because SO_2 emissions in the U.S. have decreased 15% in the past 10 years, the U.S. has already made great progress in emission control. However, she failed to take note of two other relevant facts. One is that NO_x emissions increased during this period and are expected to continue increasing in the foreseeable future. The other is that an EPA analysis, performed to estimate the cost of implementing the Senate Environment Committee bill, and several other independent analyses predict that SO_2 emissions are likely to increase in the next two decades under present regulations.

EPA's own analysis projects that national annual SO_2 emissions will go up 1.55 million tons by 1995 with much of these increases occurring in the Sunbelt states. An analysis performed by Work Group IIIB under the U.S.–Canadian Memorandum of Intent and now approved by EPA states that SO_2 emissions will go up by 850 000 tons/y, and an Edison Electric Institute analysis projects a 1.4-million

There's still not enough evidence to warrant control action.

ton/y increase by 1990. Furthermore, over the past 18 months, the Reagan administration has been pushing for changes in the Clean Air Act that would encourage even greater increases in SO_2 emissions. A more accurate appraisal of the situation would be to say that regulations implemented during the 1970s have reduced SO_2 emissions—but those same regulations will allow them to increase over the next two decades unless depressed economic conditions or other unforeseen factors come into play.

In her address to the ministerial conference, Bennett expressed "appreciation for providing us with a distillation of the research undertaken on acid deposition in Europe and North America," and went on to say that she had had "an opportunity to learn from the findings of the experts' meeting ...." Further, in emphasizing the importance of scientifically rational decision making in managing the environment, Bennett stressed the importance of diligently examining the accumulated body of scientific knowledge on the acid deposition phenomenon. At present it is not known whether the administration views the Stockholm Conference report as an important contribution to this effort or not. What is known is that Bennett directly contradicted the experts' report when she testified before the Senate Committee on Energy and Natural Resources a few weeks later in August 1982. At this time, she said: "There is no strong scientific justification for such a program [a substantial reduction in SO_2 emissions in the eastern U.S.]—there is little conclusive evidence that it would produce dramatic reductions in acid deposition or any amelioration of its effects."

Incomplete success

The ministers' conference adopted a consensus statement that is fairly strong, though nonbinding. It asserts that tall stacks are an "obsolete" control technology, calls for "further concrete action" to control transboundary air pollution, and requires that "concerted international programs for the reduction of sulfur emissions" be established. West Germany's G. R. Baum announced his government's new policy of reducing SO_2 emissions by 50% and said, "Action in environmental protection which is not taken today will cost us a lot more than [it does] today in a few years' time." Several countries that had been rather lukewarm about the idea of reducing emissions—The Netherlands, Belgium, and Aus-

tria—spoke out more strongly in favor of near-term controls.

But in the view of those countries that advocate a substantial reduction in emissions, the conference was far from a complete success because it did not agree to specifically defined objectives for polluting nations to meet in controlling their emissions, or on a timetable for such reductions. The two countries on the other side of the fence, Great Britain and the U.S., were apparently happier with the results. Kathleen Bennett held a press conference afterward at which she said she was "satisfied and pleased with the outcome."

Environmentalists would term the conference a victory in some respects. When it began, only 12 countries had ratified the UN–ECE Convention on Long-Range Transboundary Air Pollution. During the conference, many countries promised to ratify the convention. By press time, 23 out of the 24

"Acceptable" target loading recommended

For more than two years prior to the Stockholm Conference, the Swedish Ministry of Agriculture and Environment conducted an intensive analysis of available data on acid and sulfur dioxide deposition; its effects on water quality, the biosphere, and materials; and both ameliorative and mitigative control approaches. This effort culminated in a 232-page final report entitled "Acidification Today and Tomorrow," which was issued at the Stockholm Conference in four languages.

One of the most important parts of this preconference report is its recommendation of an "acceptable" target loading for protection of sensitive surface water systems: 0.3–0.5 g of total (wet plus dry) sulfur/m²·y. This "acceptable" amount is equivalent to a deposition of about 9–15 kg of wet plus dry sulfate/ha·y. The Stockholm Conference discussed an acceptable target loading but failed to reach unanimous agreement on this subject.

Copies of the English version of "Acidification Today and Tomorrow" and the Stockholm Conference Report can be obtained by writing to the Swedish Ministry of Agriculture and Environment, S-103 33, Stockholm, Sweden.

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ratifications needed to bring the convention into force had been obtained, and Austria and Switzerland were expected to ratify soon.

After ratification and a 90-day waiting period, the next meeting of the executive body of the ECE Convention will be able to take official action. At this meeting, those countries strongly favoring emissions reductions will probably try to have the consensus report, which was adopted unanimously at the ministerial meeting, incorporated as an annex to the convention, Gregory Wetstone of the Environmental Law Institute told *ES&T*. If they are successful in this effort, the consensus report will become binding on the ratifying governments.

On the negative side, environmentalists would point out that some European countries with the greatest emissions did not attend the Stockholm conference. Of the Eastern bloc, only East Germany and Hungary were there. The largest polluter, and first nation to ratify the ECE Convention, the Soviet Union, did not even show up. Environmentalists would also cite as discouraging the fact that a number of ECE member nations such as Greece, Italy, and Spain have not yet developed a strategy for controlling sulfur dioxide ambient concentrations in their own countries, let alone a way to prevent transboundary pollution.

As shown by the selected conclusions listed in the box, this conference achieved further progress in developing a scientific consensus about air pollution and acid deposition. Another estimate of "acceptable" target loadings was proposed. The effects of sulfur pollution and acid deposition on forests in central Europe were recognized and caused an important shift in attitudes of central European governments. Emphasis was given to the practical value that energy conservation and energy efficiency have for improving environmental quality. A continuing dialogue among scientists and government representatives from many countries can be expected as the Convention on Long-Range Transboundary Air Pollution moves from ratification to implementation. Notwithstanding the dramatic shift in the policies of some European nations and the growing consensus among the international scientific community, it is not apparent that the U.S. government has changed its acid rain policy. But selective listening and learning may be hard to sustain in the context of this continuing international dialogue and discussion.

—Bette Hileman

Toxicology in the Arkansas pine country

*With some unique scientific and personnel policies,
the National Center for Toxicological Research
overcame a once poor reputation to evolve into a major
federal laboratory studying the whole gamut of toxic actions
of pharmaceuticals, foodstuffs, and pollutants*

NCTR: *Studies from molecular to whole-body level*

In the last analysis, all toxicology laboratories share a common goal. They aim to establish or predict the effects of given biological or chemical materials on humans from microbial, animal, and other tests. The motives for these types of studies differ from laboratory to laboratory. For example, an industrial laboratory might aim to demonstrate that a chemical or drug that the firm wants to introduce commercially will not present an unreasonable health risk. On the other hand, a federal government laboratory, or one of its academic contractors, may seek to develop data to serve as a scientific basis on which regulatory action should, or should not, be taken.

Even within the federal establishment, toxicology laboratories, of which there are perhaps 20, differ. There are a number of such differences: the manner by which the laboratory works to forecast human effects; the lead agency to which the laboratory director reports; and the inventory of capabilities, equipment, facilities, and scientists within the laboratory. Also, like any other establishment, a laboratory is only as good as its scientists. Its personnel, especially the scientists and director, give it its character through the nature, quality, and quantity of the work done, and through the policy decisions of the director and management.

The National Center for Toxicological Research (NCTR, Jefferson, Ark.) is similar to other federal toxicological laboratories in that it shares a common goal of determining risks to human health and welfare and provides data that may be used in regulatory decision making. The way NCTR goes about determining such risks is different, however. With foodstuffs, pharmaceuticals, and environmental chemicals, this facility has to develop the necessary data for possible future regulatory activity. To carry out this task, the Center has established what is reputed to be one of the most highly computer-automated toxicology laboratories in the U.S.

Another special capability of NCTR is its ability to study long-term effects of low doses of substances on animals, with a minimum of influence of extraneous factors. "The Center does this better than most other laboratories can," Gerald Meyer, associate commissioner of the U.S. Food and Drug Administration (FDA), suggested to *ES&T*.

Still another characteristic that differentiates laboratories is found in the goals that a director may envision. For instance, NCTR director Ronald Hart wants to use the facilities and know-how of his staff to ascertain the pharmacological *mechanisms* of all types of toxic action, from the molecular and cellular to the whole-body level. He wants to know what the toxicological end point for a substance is and how the toxicant reaches that end point from entry into the cell, organ, or body, to the final effect(s).

A National Research Council staff member explains the difference by saying that some toxicological laboratories seem to concentrate more on one aspect of toxicology, such as DNA adducts or particular epidemiological effects, whereas the present NCTR policy is to try to examine as many toxicological processes as possible. Another policy is to attempt to develop means of quickly and reliably estimating which chemicals present real threats and require longer-term, more costly testing.

Growing pains

Administratively, NCTR reports to the FDA commissioner. Most of its $22 million funding for fiscal 1983, about 80%, is from FDA, with the balance furnished by other agencies through interagency agreements. The center occupies 496 acres next to the 15 500-acre U.S. Army Pine Bluff Arsenal, of which it was once a part. There are about 600 employees, 300 of whom are federal civil service and the rest contractor personnel. Until 1969, classified research on biological warfare agents took place there.

In 1969, then-President Richard

Nixon ordered an end to this research. In January 1971, he further ordered that a National Center for Toxicological Research be established under what is today the Department of Health and Human Services (HHS). The center was to take possession of the old biological warfare site at Jefferson, near Pine Bluff; HHS (then HEW) actually took title in May 1972.

Some members of the toxicology community have told *ES&T* that NCTR's beginnings and earlier history were difficult. It took eight months just to remove extremely dangerous materials with potential use as biological warfare agents and to decontaminate the facility. Also, while some portions of the facility may have been suitable for production and control of microbiological materials, the animal rooms, other spaces, and equipment were initially inadequate for toxicological research of the kind envisioned for the Center.

When the first director took up his position in 1972, "all he found at the place was dust," said W. Gary Flamm, associate director for Toxicological Sciences at FDA's Bureau of Foods and a member of the center's Science Advisory Council during 1973–80. "In the beginning, the director had to improvise a lot. What often happens then is that a lab director in that kind of a situation can end up with more than a few administrative problems and much criticism, which may or may not actually be warranted," Flamm added.

Apparently the Center did experience difficulties. In 1977, a National Academy of Sciences (NAS) team inspected the facility and expressed displeasure with its operation. Shortly thereafter, the first director left NCTR and then-FDA Commissioner Donald Kennedy appointed Tom Cairns as acting director, pending a search for a permanent director. Ronald Hart, a professor of radiology at the College of Medicine of The Ohio State University, assumed NCTR's directorship in January 1980.

The Research Scientist Group

When Hart took over, his first step was to consult with staff scientists and revitalize both the Research Scientist Group (RSG), composed of all research scientists at the Center, and the Science Council (SC), composed of all senior research scientists at NCTR. The first action of these groups was to prepare a set of operating standards for the center. These included the "Protocol Handbook," which outlines how protocols will be prepared and re-

viewed, both internally and externally, and the "Scientist Peer Review System," which is not only rigorous but external to the agency. Although the RSG's and SC's primary functions are to provide initial peer review of reports and experimental protocols, at NCTR, unlike other laboratories, they have a considerable administrative and personnel policy-making role.

Hart: learn the whole mechanism

The Center's external peer-review committee determines whether a scientist's productivity of rigorously peer-reviewable papers and protocols is sufficient to warrant that scientist's advancement or retention, or is felt to be such that the group would even recommend the scientist's demotion or dismissal. At the Center, a scientist rises or falls on such productivity, Hart said. He holds himself subject to the same policies that apply to his staff scientists concerning report and protocol development, review, and productivity. He remains an active scientist and is author or coauthor of more than 50 publications since assuming the position of director.

Another move by Hart, readily agreed to by the RSG and SC, was the phaseout, in 1981, of *all* non-peer reviewed work. Nevertheless, Center scientists are encouraged to pursue initial lines of scientific inquiry, without immediate peer review, if it is apparent that such efforts might lead to more extensive peer-reviewed work resulting in contributions to the toxicological literature, or to experimental protocol development.

Hart points to several accomplishments he feels that his policies brought about. During 1974–79, peer-reviewed publication productivity, not including abstracts, presentations, or final reports, ranged from 24 to 42 a year. For 1980, this number jumped to 130; 1981 saw 173 publications, with 180 publications projected for 1982. The number of final reports went from six in 1980 to 24 in 1981 (with 102 in

some stage of preparation by the end of 1982).

Also, while there has not been an NAS review of the Center since 1977, members of the Board of Toxicology and Environmental Health Hazards (BOTEHH) held a working meeting at NCTR in 1981. BOTEHH chairman Ronald Estabrook of the University of Texas Health Science Center at Dallas explained to *ES&T* that although this meeting did not constitute a formal NAS review with a report, many board members, including Estabrook, were personally favorably impressed with the scientific and administrative procedures put into practice since Hart assumed the NCTR directorship.

Protocol development

The emphasis at NCTR is ultimately on human health effects, but might not the same be said about other agency laboratories engaged in toxicology? For example, the National Institute of Environmental Health Science (NIEHS) has the same emphasis, at least as far as environmental contaminants are concerned. Robert Tardiff of the National Research Council says, "Yes, but NCTR does actual toxicity testing, while NIEHS does not. For instance, NIEHS is more likely to conduct research to see how carcinogenic promoters function, while NCTR, using peer-reviewed protocols, might test a foodstuff or environmental contaminant to determine if such an agent is, in fact, a promoter. In other words, NIEHS knows or suspects that there is toxicity, but NCTR actually tests for it."

Since in-house and outside peer-reviewed research is the main task performed at the Center, the quickest way for a scientist to advance is by developing a large number of high-quality, strictly peer-reviewed experimental protocols in various aspects of toxicology. This policy was adopted by Hart with his RSG and SC in 1980. Such protocols become a part of the experimental literature in toxicology.

A scientist might note that a polynuclear aromatic hydrocarbon (PAH) seems to have no carcinogenic effects, but does have a molecular structure that makes him suspect that certain metabolites of the PAH could be potently carcinogenic. The scientist would propose his concept. If it is approved by Hart and the RSG, he would become principal investigator (PI).

The scientist then searches the literature and consults with other knowledgeable people in his field, in and out of the Center, to learn what, if

NCTR organization

Office of Scientific Intelligence	Director	Quality Assurance Staff

Associate Director for Chemical Evaluation		Associate Director for Research		Office of Management	
Division of Chemical Toxicology	Nutrition Chemical and Evaluation Branch	Division of Carcinogenesis Research		Planning and Evaluation Staff	
	Diet Preparation Branch	Division of Mutagenesis Research		Division of Toxicological Data Management Systems	
Division of Pathology		Division of Teratogenesis Research	Pharmacodynamics Branch	Division of Management Services	
Division of Animal Husbandry			Perinatal and Postnatal Evaluation Branch	Division of Facilities Engineering and Maintenance	
Division of Microbiological Services	Bacteriology Branch		Developmental Mechanisms Branch		
	Virology Branch	Division of Biometry			
		Division of Chemistry	Diet Analysis Branch		
			Analytical Methods Branch		
			Spectroscopic Techniques Branch		
		Division of Molecular Biology	Immunotoxicology Branch		
			Cell Biology Branch		

any, other work was done on this particular PAH. Next, as PI, he prepares a proposal paper that sets forth the goal of the proposed research, preferably with a beginning hypothesis that can be tested experimentally. The PI also lists specific "milestones" he expects to reach, with a projected timetable for reaching them.

The paper would cite deficiencies in knowledge—in this case, about the PAH compound and its metabolite(s). It includes any restrictions or limitations there may be on the scope of the PI's research. For example, limits can be imposed by an outside organization sponsoring such research.

Experimental methods are listed, along with the rationale for choosing these methods, including possible shortcomings or limitations, alternative approaches, and, as necessary, procedures for compliance with any OSHA, Good Laboratory Practices (GLPs), and other federal regulations that may apply. The Center is in a good position to judge GLPs, since it helped to train nearly 600 GLP inspectors for FDA, EPA, and two other agencies, since 1976. Finally, benefits (especially those health related ones), innovations, expected costs, and other pertinent information are documented.

The first review is by the internal RSG for scientific validity; a further review covers safety and GLP evaluation. Given favorable comments from the RSG, which itself consists of principal investigators, the next reviewers are senior scientists comprising NCTR's Science Council. After council approval, the protocol is sent to Hart. Even if he likes the protocol plan, he will most likely send it for further assessment to government or academic experts outside the Center, of which NCTR uses about 200.

If the outside peer review, which is conducted by three to seven internationally recognized scientists, achieves a score of "excellent," resources are allocated; the results, positive or negative, are used as part of the "Scientist Peer Review System," which helps to determine one's rank and advancement at the Center. Moreover, after a protocol has been carried out, all final reports are subject to the same rigid in-house and outside peer-review process.

In addition, NCTR has an outside Science Advisory Council (SAC), to which the University of Texas's Estabrook was recently appointed. However, Estabrook told *ES&T* that to his knowledge, this SAC has not met in recent years to give the Center a "needed input by outside reviewers." However, he expressed his hope that Hart would welcome a meeting of this group of scientists "to help him evaluate the activities at NCTR."

Short-term tests wanted

Experimental know-how built up from sound protocol development can help to reduce the difficulties, time, cost, and general "pain" involved in conducting research on toxic substances. Without this know-how the sheer number of chemicals needing testing could swamp the capabilities not only of NCTR, but of all laboratories equipped to do such work. Another problem facing researchers is budgets of increasing austerity. Thus, new methods and a better understanding of ways to detoxify, or predict the toxicity of compounds on human populations "are desperately needed," Hart says.

Long-term, low-dose testing of single chemicals, or even combinations of chemicals, on a large number of animals for the fullest possible picture of toxic effects from molecular to whole-body level is a special NCTR capability. But while such tests can certainly lead to thorough knowledge, they cannot keep up with the need for tests. In Hart's view, shorter-term tests are needed. Results from shorter-term tests could indicate the compounds that require longer-term tests. To save time and money, and to increase effi-

ciency, Hart wants to develop methodologies that could *predict* toxic effects at various levels. These predictions might also suggest longer-term, more extensive studies.

This development of valid short-term tests would be in conformity with the objectives of the National Toxicology Program (NTP); NIEHS is the lead agency of NTP and the Center is a major participant. In fiscal 1981, about $7 million, or one-third of NCTR's total budget went into NTP work. One aim of the program is the testing of selected compounds that are widely used and may have public health implications. Examples include caffeine, gentian violet, and certain antihistamines.

Other NTP efforts encompass chromosomal/genetic damage, carcinogenicity, teratogenicity, and routes of exposure to chemicals that might engender these effects. In addition to these types of studies, Hart hopes the center will gain more knowledge of genetic repair mechanisms and develop valid experimental protocols for determining how DNA repair might be brought about.

The "A Barrier"

For testing at NCTR, there is a tremendous array of analytical chemistry instrumentation, animal care/feeding/diet set-ups and rooms, and pathology facilities. There are, for instance, advanced gas, high-performance liquid, and thin-layer chromatographic instruments, nuclear magnetic resonance (NMR) and mass spectrometers (MS), and specific pathogen-free rodent breeding facilities (13 rooms, 517 ft^2/room). The Center also has a 100-animal primate breeding colony.

The newest NMR spectrometer at the Center is a powerful 500-kHz unit that cost about $550 000—"a little over $1000/kHz," Ron Mitchum, director of NCTR's Division of Chemistry, said. He explained that this device will detect minute traces of toxic organics that can be more precisely quantified by other means. What about a triple-quadrupole MS? "We don't have one right now," Mitchum said. "But when we need a triple-quadrupole, we don't plan to acquire one, since we have the people and know-how to design and build it ourselves."

Facilities to synthesize chemicals under rigorous safety conditions are available. For example, to run large-scale, low-dose tests of a PAH metabolite—e.g., 7-methylbenz[*a*]anthracene-*trans*-7,8-diol-*anti*-9,10-epoxide—one needs *gram* quantities of this substance to feed to many animals. This metabolite, a suspected "proximate" or "ultimate" carcinogen, would exist in an animal's body in nanogram amounts. At NCTR, compounds such as these can be synthesized in the needed quantities in laboratories that are constructed so that scientists and technicians—specially garbed, as necessary—do not come into contact with such chemicals. Properly sealed in a vial, this particular metabolite would probably appear as a nondescript, innocent-looking white powder.

Another facility is the "A Barrier" comprising 21 rooms totaling 35 000 ft^2. Not only is it kept pathogen-free, but air, water, light, temperature, humidity, and other factors are strictly controlled by a center-wide computer monitoring system. Anything—human or animal—entering goes through decontamination. Scientists and others must brush their teeth, gargle, shower, and wear sterile work clothes, including a surgeon's mask. People with access to the "A Barrier" are subject to complete periodic physical examinations. A filtering system captures virtually all bacteria, viruses, particles, and airborne chemicals. Personnel move from cleanest to less clean rooms with no retracing of steps.

The Center has garnered much know-how about animal diets and about the precise metering of a chemical or group of chemicals to be administered. One example is a large rodent feeder that greatly reduces spillage and loss; it has been used in an experiment involving 24 000 mice. Another approach to ingestive feeding could remove the need for gavage, a painful method of administering discrete amounts of substances through a tube passed through the animal's trachea. The tube carrying the material to be tested goes directly to the animal's stomach. In some cases, gavage can actually kill the animal. To prevent this, NCTR is evaluating the feasibility of microencapsulation of the test chemical(s), which are then mixed in the animal's food. The capsule readily dissolves in the animal's gastric system, allowing the chemical access to the animal's body in the desired amount.

Lines of defense

There are other modern, sophisticated equipment items, along with the scientists and technicians qualified to operate them. They are all being used to learn all that is possible about how and why a given material or material combination is toxic. This work includes studies in mutagenicity, teratogenicity, carcinogenicity, and acute toxicity, from minor impairments of body function to lethality.

Hart believes that with such thorough knowledge, lines of defense can be built up. They vary from technical and regulatory steps for minimizing exposure to devising corrective measures that could be taken if it is suspected that exposure has occurred. He envisions countermeasures that could run the gamut from improved means of detoxification at whole-body level to interrupting carcinogenesis mechanisms and finding ways of bringing about repairs at chromosomal, genetic, and DNA levels. —Julian Josephson

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Chemical studies at NCTR in 1981

Type of study	Number of chemicals studied [a]	Example of chemical used for study
Acute/chronic	20	Lindane
Biochemical/cellular/tissue effects	106	Dibenz[*a*]anthracene-*trans*-3,4-diol
Carcinogenesis	63	Benzo[*a*]pyrene
Immunologic toxicity	27	Chloroacetic acid
Mutagenesis/genetic toxicity	44	Dimethylnitrosamine
Neurologic/behavioral toxicity	5	Methylmercury
Nutritional studies	1	2-Acetylaminofluorene
Pharmacokinetics/metabolism	111	Phenanthrene
Reproductive/developmental toxicity	28	Carbon disulfide
Systemic/organ toxicity	9	[^{3}H]4-Nitrobiphenyl
Chemistry	149	(^{13}C) TCDD

[a] Some chemicals may have been used in more than one type of study.
Source: NCTR

Regulatory reform legislation

Michael R. Deland

A veritable explosion in governmental regulatory activity has occurred in the past 20 years. The number of state regulatory agencies increased from 150 in 1960 to 1500 in 1979. Since 1969, 26 new federal agencies have been created, including the Occupational Safety and Health Administration, the Consumer Protection Agency, and EPA.

The volume of regulations also has proliferated. In 1960 there were 14 000 pages in the *Federal Register*, by 1970 the number had grown to 20 000, and by 1980 to 87 000. (President Reagan's regulatory reform program reversed this trend, and by 1981 the pages had been reduced to 64 000.)

The costs created by regulations have soared concurrently and are now estimated by the business community to be $100 billion or more per year. While it is widely recognized that the costs of not regulating also can be substantial, as evidenced by the Love Canal tragedy, there is clearly a consensus that some form of regulatory reform is needed.

The procedures by which agencies promulgate regulations are still governed by the Administrative Procedure Act (APA), which was passed in 1946—long before the sweeping change in the nature and reach of agency rule making. In the past five years, both Democratic and Republi-can administrations have pushed for regulatory reform legislation, and two successive Congresses have debated it, thus far without final enactment. On March 24, 1982, the Senate passed a regulatory reform bill by a 94–0 vote, but despite strong bipartisan support and designation by President Reagan as a top priority for the lame-duck session, a comparable version (H.R. 746) has yet to pass the House.

Legislative goals

The reform effort is supported by a broad business coalition and by groups such as the American Bar Association. The major goal of the legislation as envisioned by these groups is to force the regulatory agencies to be accountable—to justify on the record their regulatory initiatives. If this is done, the quality of agency decision making should improve.

The proposed bills, which pertain only to "major" rules (defined as those that have an annual impact on the economy of $100 million or more), seek to accomplish this goal by several means. First, agencies would be required to analyze whether the rule is needed and to set forth the benefits it is likely to achieve, along with the adverse effects it is likely to produce. Agencies also would be required to identify and analyze reasonable alternatives and to evaluate their merits against the proposed rule. Second, the opportunity for public participation in the rule-making process would be expanded by providing an opportunity for oral presentation and for limited cross-examination.

Another key element of the current House compromise bill is the Bumpers Amendment, named after its chief sponsor, Sen. Dale Bumpers (D-Ark.). Under existing law, the exercise of agency discretion can be successfully contested only if it can be shown to be "arbitrary and capricious." The amendment would make it easier to challenge an agency regulation by requiring that the agency have "substantial support" in its rule-making file to justify its action and to avoid an arbitrary and capricious finding.

Major objections

Opponents of the legislation include many environmental, consumer, and labor groups, who fear that regulatory reform could be a "back-door way" to weaken protection of public health, safety, and the environment. Their cause is championed in Congress by House Energy Chairman John Dingell (D-Mich.), who, while strongly supporting "the notion of genuine regulatory reform," believes the current bill is a "hodgepodge" of concepts and proposals that would result not in reform but in "further delays and new opportunities to challenge often needed health, safety . . . and other essential regulations."

Opponents of the bill have three major objections. First, they feel that the legislation would impose so many procedural steps on agencies that it would "bog down" the regulatory process. Second, they say a reliance on cost–benefit analysis, however modified, "inevitably skews a decision in favor of costs" since they are easier to quantify than benefits. Finally, the opponents strongly object to giving the Office of Management and Budget any statutory authority to "interfere in the regulatory process," particularly that of the independent agencies.

Regulatory conditions today are dramatically different than they were 36 years ago when the APA was enacted. Few question that regulatory reform is needed; and Congress, after four years of debate, should be prepared to participate creatively in the reform process.

Deland writes this column monthly and is counsel to ERT, Concord, Mass.

Commercializing biomass conversion

*Here are some of the methods, prospects, and problems
involved in converting plant material. Although energy production
presently generates more interest, perhaps the first aim should be
toward making organic products with higher profit potential*

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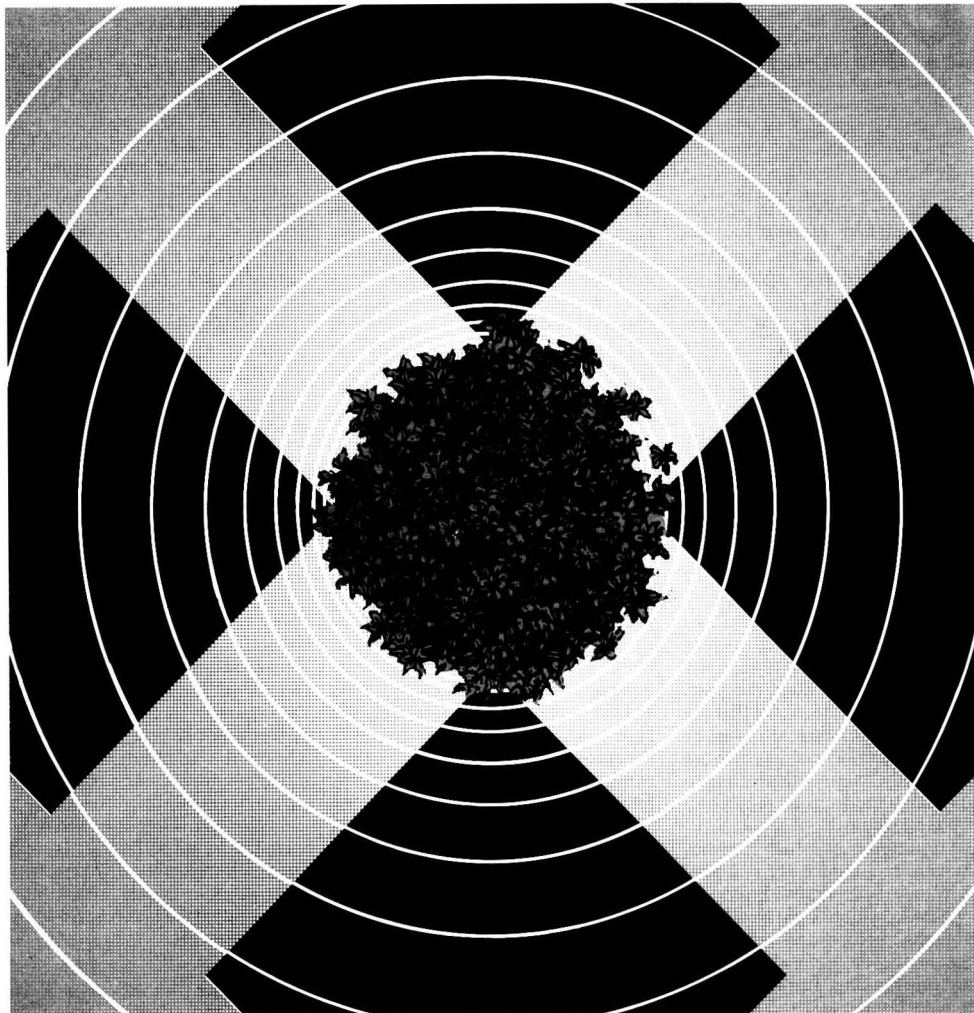
Many of the oil-importing nations of the world are fighting for economic survival because fuel costs are rapidly draining their financial resources. While not in such desperate economic straits, the U.S. also suffers from the high cost of imported petroleum.

Recently there has been a virtual halt in oil price increases; this can be ascribed to several factors. These include a decline in world demand, brought about by a business recession; better performance of motor vehicles with respect to mileage per gallon of fuel used; and more efficient use of fuels in factories and homes. However, this pause in petroleum price increases is probably temporary.

Therefore, alternatives must be examined, and biomass as a feedstock for fuel and chemical industries is one option that has attractive prospects. Initially, perhaps, biomass industries will be small factors in large markets keyed to expensive fossil feedstocks; nevertheless, there should be opportunities for sizable profits. It is also expected that products made from biomass can be priced at competitive levels.

Biomass, created mainly through photosynthesis, is one of nature's "techniques" for utilizing solar energy. Most other technologies for harnessing the sun's energy present formidable engineering problems. For example, photovoltaic devices are expensive to construct; they require maintenance; and they must have provisions for energy storage for times when the sun is not shining. Mounting solar converters in space and beaming microwave energy continuously to the earth is far too expensive—especially when the microwave intensity may be roughly the same as that of sunlight—and could be hazardous. On the other hand, boilers powered by focused sunlight, wind energy, generation of electricity using thermal differences in the oceans, wave energy, and other means of direct or indirect harnessing of solar energy could make significant contributions if and when economic and logistical conditions are favorable, but it is hard to predict when such favorable conditions may be achieved.

For these and many other reasons, biomass has some very attractive features. For instance, no backup system is needed for energy storage. Biomass is quite reactive, especially when it consists of sugary or starchy materials. Since many different plants constituting biomass are roughly equivalent in energy potential, no one plant need have an exclusive market; thus, because of the diversity of resources, cellulosic materials may be expected to have stable prices. Finally, the agricultural technology for growing biomass is essentially well established. However, biomass resources are very diffuse, as compared to concentrated deposits of coal, oil, and gas; biomass has a high moisture content that results in higher mass and lower fuel value; and the most promising conversion technologies need further research and development.

In the U.S. and several other countries, there is ample biomass; its rate of growth is appreciably greater than the rate of fossil fuel consumption. Nevertheless, there are formidable obstacles to biomass utilization. First of all, nutrients for new growth are provided to the soil as plants comprising natural growth decay and die. Soil fertility may decline rapidly if we intercept the growth and take from the land without returning nutrients such as organic matter, nitrogen compounds, and phosphate to it. Amounts of biomass can increase dramatically with fast-growing species and sound management, but there are maxima in growth rates and in the efficiency of capturing sunlight. In addition, in few areas of the world is water so abundant that its cost can be neglected. Moreover, fertile soils are needed to grow food. Nevertheless, there are sufficient resources now to allow large biomass industries to get under way. Indeed, many farms of the future may produce food, fiber, and energy feedstocks.

There would be little merit in biomass fuels if the percentage of their contribution to the total available energy declines while the total demand for all energy keeps on soaring. However, all sources of energy have limitations, and none can keep up with an insatiable demand. It is likely, therefore, that energy costs will become so high that nations must approach an energy demand ceiling under which biomass can become a key contributor.

Energy businesses today collect fossil gas, coal, and oil, then subject them to a minimal cleanup and rearrangement to produce cheap fuels. A competing biomass industry should not need sophisticated processing in order to obtain products similar to the feedstocks of today's energy industries.

Actually, biomass conversion could probably achieve commercial success much sooner if it focused on more valuable, high-quality fuels and chemicals rather than on cheap substitutes for gas and heating oil.

Biomass factories have an upper limit on size, because feedstock logistics are critical. Hauling costs are significant; thus, a reasonable size might be based on fitting loading, hauling, and unloading into normal work shifts. Distances allowing two round trips per truck per day would be attractive. A factory processing 1000 tons/d (dry basis) seems to be a good compromise, big enough to realize economies of scale, while drawing feedstock from a 50–80-km radius to keep hauling costs in line. Per unit of product, it can cost several times as much to build a small plant, so large factories would have a distinct advantage.

Feedstocks

Terrestrial plants. The cost of land must be affordable, and there must be suitable soil and climate. Future fertilizer and water costs are unpredictable; biological fixation of nitrogen and recycling of phosphates and of water could stabilize the costs for biomass plantations. It is difficult to estimate real cost when there are subsidies, depletion allowances, tax incentives, supports in the form of government-built highways, etc., but biomass industries will resemble agribusiness, with variations caused by weather and market interplays. Thus, the pattern of costs should be steady except for these perturbations.

New multipurpose crops that supply food, fiber, and chemicals can revolutionize agriculture, but existing biomass can lead the way. Many nations have enough trees to supply a large bioconversion program, although most agricultural residues are presently put to poor use. Usually, residues are left on the ground to rot and thus provide some erosion control and feed some organic matter back to the soil. As these residues are diverted to bioconversion, new methods of soil management must be devised.

Some of the new crops being studied have exciting prospects. For example, mimosa is a woody legume that derives much of its nitrogen from the air. Several plants with reasonably high productivity can thrive in alkaline soils, and some tolerate quite brackish water. This would allow some lands now considered useless to be employed for cultivating biomass.

Aquatic plants. Plants grown in water can utilize areas not committed

to other purposes. Fresh waters are usually part of reservoir, shipping, or recreational systems, but there may be opportunities for growing biomass. Certainly, streams naturally choked by water hyacinths might be dedicated to biomass production. Lakes, streams, marshes, and freshwater impoundments can be used to grow many different plants, but floating species offer advantages for easy harvesting. *Hydrilla*, duckweed, and various algae show promise, and water hyacinth is very productive in hot climates. Of the rooted plants, cattails are particularly attractive because of their wide geographic range and high productivity.

Several aquatic plants can convert nitrogen in the atmosphere to organic nitrogenous compounds. This can eliminate or greatly reduce the need for fertilizer. In India, nitrogen-fixing algae are grown in very shallow ponds and allowed to dry; they are then used as fertilizer. It is also common in Asia to grow the water fern *Azolla* that has internal symbiotic algae. *Azolla* is the most efficient known fixer of atmospheric nitrogen and produces excellent fertilizer for rice fields; it might itself be a good food or feedstock for fuels and chemicals.

Marine plants have high maximum growth rates, and the open oceans offer vast growing areas. Unfortunately, the ocean surfaces are too low in nutrients. Nevertheless, there are schemes to anchor giant kelp in the oceans and to use wave action to pump nutrient-laden water from the depths. Indeed, proponents of kelp cultivation have forecast wildly optimistic yields and have minimized the problems of kelp nutrition and of economical processing. Some aspects of the U.S. Department of Energy's projects with kelp developed into a scandal (1).

A floating marine plant with great potential is *Sargassum;* it grows in relatively shallow waters that hold nutritious sediments that would settle in the open oceans, and it might be harvested by wind action. Also, some other algae excrete oils or waxes when the nitrogen supply is limited, but their production rates are poor. Perhaps genetic modifications might result in strains with good productivity.

Plants containing sugars or starch. Land plants that produce sugars are well-known (sugarcane, maple trees, sorghum, and sugar beets). The sugars are used mostly as food, but many chemicals can be derived from them. Starchy plants, such as corn, potatoes, and cassava, are also important foods. In the U.S., in addition to food needs, there is sufficient corn that can be al-

located to fermentation for ethanol production. However, the economics of corn alcohol would be rather unattractive without government incentives.

Plant exudates. Rubber is produced on tree plantations, but guayule is considered a promising alternative. Many plants contain latex or suspensions of steroids, waxes, or hydrocarbons. Most such plants are found in arid regions and tend to have low growth rates. However, modern genetics may transform them into miniature chemical factories. Plants that produce hydrocarbons or chemicals directly have an exciting future for rubber and high-value organic compounds, but not for cheap fuels.

Exudates from coniferous trees such as pine seem to have been overlooked as potential major replacements for petrochemicals. Applying the herbicide paraquat to pine trees stimulates production of up to 10 times more resin and turpentine than is normally produced, and the yields are in excess of the most optimistic estimates for exudates from arid-land plants on a per hectare basis. If the wood and pine chemicals are valuable coproducts, quite profitable operations are possible. The existing industry, known as gum naval stores, has been in sharp decline because of obsolete technology and high labor costs, so new methods would be important for exploiting the greatly increased yields of exudates (2).

Energy cane. Until very recently, only the sucrose in sugarcane attracted commercial interest. Strains were chosen for the highest yield of sugar at the lowest cost. Many other strains that produced excessive leaves or stalks were shelved or discarded.

Prior to cutting, the practice in many countries is still to burn the leaves; this creates air pollution and can be hazardous because sudden high winds can spread the flames and devastate adjacent fields. The residue remaining after the sugar is extracted, bagasse, is still discarded at some sugar refineries, although most now use it to replace expensive boiler fuels.

In Puerto Rico, there is an exciting program to grow "energy cane," using sugarcane varieties that produce roughly the same amount of sugar as do customary varieties but with about twice as much total biomass (3). Such a crop could provide a reasonable sugar yield plus boiler fuel far in excess of the needs of the sugar refinery. This extra biomass is fully satisfactory as fuel for generation of electric power, once it is dried and reduced to a parti-

cle size easy to handle and burn. The economy of the island of Puerto Rico has suffered greatly from increases in the price of oil, so lower cost fuel from energy cane is very attractive.

Thermochemical conversion

Woody plants were the fuels for primitive humans. Plants used as firewood have been surveyed, and shifting to different species could increase wood availability in many areas of the world (4). The present technology for burning wood ranges from an open fire on the ground to very modern, fluidized-bed combustion of sized and dried particles.

Even highly developed nations derive significant benefit from wood for heating homes and generating power. Furthermore, biomass is low in sulfur and requires less pollution control equipment than does the burning of coal. Although wood combustion can meet needs for cooking and for heating of homes, there would be a benefit from more efficient burning in large power plants. This improvement must be balanced against the cost of distribution systems and power line losses.

A problem with wood burning is the greater air pollution generated by many small, inefficient fireplaces. If firewood is dried or pelletized, better combustion more than repays the cost and energy of treatment.

Thermochemical conversion of biomass to fuels and chemicals is derived from technologies used for coal. Biomass is widely distributed and cannot achieve economies of scale anywhere near those of very large coal conversion factories, but biomass is quite reactive and may be less costly to process. Practically any carbonaceous feedstock is suitable for thermochemical conversion.

Options are gasification, pyrolysis, and liquefaction. Pyrolysis of biomass was important commercially until it was displaced by less costly conversions of petroleum in the 1930s. The products of pyrolysis are organic liquids such as acetone, acetic acid, and various alcohols; tar; and char. Liquefaction of biomass requires high temperatures and pressures, and the capital investment and operating costs are quite high. Neither of these thermochemical conversions can be considered competitive with gasification at present.

There has been much more research on conversion of coal than on biomass, and experiences with large-scale gasification such as the SASOL process in South Africa can be evaluated by other nations. This process leads to

synthesis gas, a mixture of carbon monoxide and hydrogen, which can be used to make many different chemicals. Methanol is the leading candidate for a fuel product, and ammonia made with nitrogen from air plus hydrogen from synthesis gas would fit into a biomass cycle as fertilizer. At present, natural gas is the preferred feedstock for synthesis gas even though coal is cheaper, because handling is simple for gas, whereas coal presents cleanup problems. Biomass would have to be relatively inexpensive—probably less expensive than coal—to become the feedstock of choice, because it is bulky, widely distributed, and costly to collect.

There have been numerous designs of gasifiers for biomass; most of the effort has been directed toward fairly small units. It seems that engineers recognize the scale required for really economic operation, but think of gasifying biomass mainly as an auxiliary operation in connection with the disposal of surplus material. For example, several small gasifiers are designed to use piles of wastes to generate low-BTU gas for local use. Very large gasifiers for coal can be future models for biomass, but small gasifiers are not yet a particularly attractive investment.

A typical design of a gasifier is shown in Figure 1. Countercurrent flow provides heat economy in that the hot gas warms the incoming feedstock. Figure 2 shows the effects of scale and feedstock cost on the required price of the product gas (5). By comparison, natural gas costs about $6/million Btu, and wood chips cost about $30/ton. It does not seem, therefore, that gasification of wood chips is profitable at present. Very large installations are required to achieve a respectable return on investment. This very large scale also implies considerable risk, and private companies are reluctant to commit themselves to such a major expenditure without government help or loan guarantees. Even the South African ventures are unattractive in the present financial climate; their production of liquid fuels was motivated mainly by the need to be more independent of oil suppliers with hostile political views.

Anaerobic digestion

Conversion by anaerobic digestion seems very attractive, since the process uses simple equipment and little control. However, there has been widespread dissatisfaction with anaerobic digestion in closely related operations with sewage sludges, because the mi-

FIGURE 1
Gasifier schematics

Updraft gasifier

Tar + H_2O
$C + CO_2 \longrightarrow 2CO$
$C + H_2O \longrightarrow CO + H_2$
$C + O_2 \longrightarrow CO_2$

Downdraft gasifier

Tar + H_2O
$C + O_2 \longrightarrow CO_2$
$C + CO_2 \longrightarrow 2CO$
$C + H_2O \longrightarrow CO + H_2$

FIGURE 2
Production of synthetic natural gas (SNG) from wood[a]

^{a}By direct gasification and combined shift/methanation, with effect of plant size on revenue required from the sale of SNG by a regulated producer
Courtesy of National Technical Information Service. Reference 5

crobial cultures are easily upset. An anaerobic digestor for fuel gas must overcome the problem of microbial culture inhibition if reliability is to be ensured. Furthermore, the product gas is roughly two-thirds methane and one-third carbon dioxide, which must be removed to bring the heating value to that of pipeline gas. This requires an investment in a relatively sophisticated purification process.

Several countries have had major programs for generation of methane gas with moderate heating value by the small-scale digestion of manures or organic wastes. China reports fair success, but the efforts in India have had a less favorable outcome. Individual farmers often have insufficient manure to warrant constructing a digester, so several must band together. Fair distribution of gas and of the sludge as fertilizer is difficult to achieve. In any event, some installations have been abandoned as not worth the effort, while others appear to work reasonably well.

Still, prospects for anaerobic digestion are improving because of new reactor designs such as those with beds packed with organisms. There have been reports of methane of 90% purity from digesters packed with immobilized organisms. This would eliminate the gas purification steps. Pretreatment aids digestion, but such pretreatments are much the same as those for cellulose hydrolysis processes that lead to more valuable products.

Digestion to produce materials other than methane seems sensible. For example, heavily loaded digesters tend to accumulate organic acids, and the production of methane is inhibited. However, such short-chain acids have reasonable value, although isolating them from crude mixtures would be expensive. While anaerobic digestion to methane might be profitable when the feedstock is cheap, a better return

on investment should result from aiming at a more valuable product.

The most likely arrangement for digestion of biomass is a two-stage, thermophilic digester. Packed-bed digesters may soon be used commercially, but there are construction details and mass transfer problems that need more study. A rough economic analysis is given in Table 1 (6). Scale-up is less of a problem for anaerobic processes than for thermochemical processes, because the reactors probably will be of a fixed large size. More modules could be added to scale up to any desired production rate, and the economies of scale could be relatively modest.

Cellulose hydrolysis

Hydrolysis of hemicellulose to mono- and oligosaccharides is easily accomplished with either acids or enzymes. On the other hand, natural cellulose resists hydrolysis for two reasons—its highly ordered crystalline structure and a physical barrier of lignin surrounding cellulose fibers. However, some of the most striking advances for the programs supported by the U.S. Department of Energy have involved various pretreatments that render cellulose amenable to easy hydrolysis.

The approximate composition of lignocellulosic materials is: cellulose—25-50%; hemicellulose—20-35%; and lignin—18-35%. Each major component should be converted to products to maximize income and to minimize waste treatment costs.

Acid hydrolysis. Acid hydrolysis of wood is an old technology; projects during World War II led to the Madison process, which optimized time, temperature, and acid strength. While the process is not economical in the U.S., other countries, particularly the U.S.S.R., have many plants for hydrolyzing wood to sugars. A few plants

produce alcohol by fermenting the sugar, but single-cell protein for animal feed is the most common product. Furfural is sometimes derived from the breakdown of the pentose fraction of hemicellulose.

Acid hydrolysis leads to a sequence of reactions. Hydrolysis is approximately 1000 times faster for hemicellulose than for cellulose. The sugars from each are degraded by acid to resins, polymers, and furfural derivatives. Reaction conditions are thus set for a compromise between hydrolysis and degradation such that the final mixture contains unreacted biomass, unwanted products, and the desired sugars. Since the sugars from hemicellulose are formed early, there is time for considerable degradation leading to major losses. With sulfuric acid, which is normally used, the maximum yield of fermentable sugars is about 55% by weight of starting cellulose. Better performance is obtained with other acids, and methods are being developed for more economical recovery of these more expensive acids.

Hemicellulose can be removed by dilute acid treatment with very little effect on the cellulose. Bacteria, molds, and yeast ferment these sugars, consisting mainly of xylose, to ethanol, but other products are usually present, and poor microbial tolerance of ethanol prevents its accumulation. An enzyme can be added to form xylulose from xylose; common yeast then ferments xylulose to ethanol in excellent yields. This enzyme is identical with glucose isomerase, which is relatively inexpensive due to its widespread use in converting glucose to high-fructose syrups for commercial sweeteners. A serious drawback is the need to recycle unreacted xylose back from the fermentation step to the enzyme to approach again the concentrations of the equilibrium mixture.

Several groups of scientists have created yeast strains that have isomerase activity and thus need no supplemental enzyme. Furthermore, organisms that have the inherent ability to ferment xylose may be so improved by mutation and selection that they merit commercial consideration. Utilizing hemicellulose to produce additional ethanol could lead to a 50-70% improvement in productivity in factories using biomass.

Direct bioconversion to ethanol. Using expensive enzymes to hydrolyze cellulose to glucose for fermentation could become obsolete before its first commercial tests, if a project at the Massachusetts Institute of Technology (MIT) is successful. Normally, the

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TABLE 1

Economics of anaerobic digestion to methane[a]

% Conversion	Required price for product gas	
	$/million Btu	$/gigajoule
30	39	38
40	24	23
60	13	13

Assumptions: Lignocellulosic feedstock at $27.50/dry metric ton

   Cost of purifying methane not considered

   Plant size is 454 metric tons/d of feedstock

   15% yearly return on investment

Note that the present price of natural gas is more than $6/million Btu.

[a] Based on an article by Jones (6)

concept involves direct fermentation and hydrolysis of cellulose and hemicellulose to sugars, with anaerobic organisms that continue fermenting the sugars to ethanol (7). The greatest single expense of other processes is production of cellulase enzymes, because this aerobic fermentation requires intense, costly mixing steps and massive amounts of air.

The MIT process is relatively inexpensive, because there is little mixing and no aeration. Coarsely shredded biomass (corn stalk and leaf residue seem best at present) is contacted with a mold culture that hydrolyzes both the cellulose and hemicellulose, but ferments only the resulting glucose. A second organism is added later to ferment sugars from hemicellulose to ethanol. Unreacted feedstock is dried and burned for power. Since the process is simple, and there is little investment in treating the feedstock, profits are possible with a low conversion to products.

A mutational program has developed microbial cultures that produce mostly ethanol and few by-products when grown on purified cellulose. Practical feedstocks do not work as well, and too much acetic acid is produced. However, improvement of the culture should solve this problem.

If conversion of cellulose is too low, burning of the residue produces much more power than is needed for the process. Selling excess steam or electric power may not be very profitable unless utility companies have an urgent need for supplemental power.

Enzymatic hydrolysis. Until very recently, neither acid hydrolysis nor enzymatic hydrolysis of biomass appeared likely to be an outstanding commercial success. Rates of enzymatic hydrolysis of cellulose are very slow unless the feedstock is pretreated. Fortunately, some effective new pretreatments lead to enzymatic cellulose hydrolysis with yields of over 90% of the theoretical amount of glucose. As costs of enzymes continue to drop dramatically, enzymatic hydrolysis is likely to become highly profitable. High titers of enzyme are produced by new strains of the mold, and there is no need for an enzyme purification step. The filtered broth can be diluted and added directly to the hydrolysis reactor.

Molds that produce cellulase have been studied intensively by Reese, Mandels, and their co-workers at the U.S. Army Natick Research Laboratories. These efforts, plus contributions of other groups (especially at Rutgers University), have created excellent new strains. A modification of the Natick process, developed at the University of California, Berkeley, has contributed engineering improvements and alternative treatments.

The Gulf Oil Chemicals Company developed an interesting process; however, it has terminated research and development and donated the rights to the University of Arkansas. Work is continuing on simultaneous saccharification and ethanol fermentation in which sugars do not accumulate to slow enzyme rates by feedback inhibition. Municipal solid wastes are to be used, and credits are taken for waste disposal when costs are estimated.

There seems to be some difficulty with reducing the feedstock to a size suitable for bioconversion; in one design of a factory, ball milling accounted for over one-third of the capital cost. But Natick workers showed that two-roll wet milling is effective with waste paper and less expensive than milling or grinding.

Residues from the Arkansas experiments have been fed to animals. However, it is unlikely that regulatory agencies would approve the meat of such animals for human consumption, because toxic material could carry through from the wastes.

The success of biomass refineries depends upon converting all of the major components to valuable products. Despite vast markets for ethanol, sales of ethanol alone probably will not generate sufficient revenue for profitable operation. Also, inability to find buyers for the large amounts of lignin produced could be an additional economic limit for the process. On the other hand, lignin burns well, and could defray most, or all, of the fuel costs of a refinery. In addition, availability of large amounts of relatively inexpensive lignin should be a stimulus to find more valuable uses.

Processes that focus on lignin

For some years, there has been interest in solvent pulping; that is, in removing lignin from wood fibers by extraction with an organic solvent. The lignin is not damaged and might command a premium price as a substitute for phenol in phenolformaldehyde plastics, or for various formulations such as adhesives and oil well drilling muds. With lignin and products from hemicellulose to defray costs, solvent pulping might compete with traditional pulping methods. The problem is efficient recovery of expensive solvents, and this is complicated by absorption into the cellulose fraction of the wood fibers.

Two different groups have disclosed processes for solvent pulping with an emphasis on lignin recovery. Each yields several products and uses mild treatment, so that the lignin fractions are relatively unaffected and remain reactive. Such lignin is much superior to damaged, substituted material from paper pulping by the conventional kraft or sulfite processes.

The Biological Energy Corporation, a collaborative effort of the General Electric Company, the University of Pennsylvania, Hahneman Medical Center, and Lehigh University, uses alcoholic solvents with acid or alkali to extract lignin from wood chips, while simultaneously hydrolyzing the hemicellulose to soluble mixed sugars. Lignin precipitates as the extract is evaporated to a sugar syrup, and the vapors go to solvent recovery. The solids from the wood chip extraction are cellulose with desirable properties for use in paper. However, commercial success hinges on excellent solvent recovery, and it is not easy to remove the last traces of solvent from the cellulose.

The other pulping process is owned by Battelle—Geneva, and differs primarily in that phenol, instead of alcohol, is used. Hot water and phenol are miscible and dissolve lignin while hydrolyzing the hemicellulose. On cooling, a water-rich layer forms that contains the sugars; the lignin is in the phenol-rich layer. Again, a key economic factor is recovery, and phenol, with a higher boiling point than common alcohols, is more difficult to recover. Basics of solvent refining are shown in Figure 3.

Economic information that has been released by Battelle—Geneva is in Table 2 (8). The plant cost is roughly the same for other processes for refining lignocellulosic materials.

Steam explosion of wood chips to make Masonite, a filler for construction materials, is well known. The cellular structure of wood is impregnated with steam, and is disintegrated when the steam is suddenly expanded. Cellulose fibers are shortened and weakened, so there is little prospect of manufacturing good paper products by steam explosion. A Canadian company, Stake Technology, has a continuous process using a mechanical screw plus steam for exploding wood chips. Cattle can digest this product more easily than wood, and it could be fractionated to lignin and to hemicellulose sugars and cellulose.

However, another Canadian company, Iotech, has viewed steam ex-

FIGURE 3
Solvent pulping
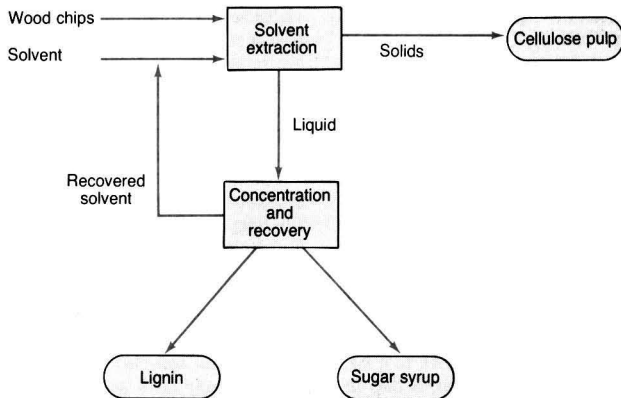
TABLE 2
Economics of solvent pulping

Battelle—Geneva process (derived from information in Reference 8)

Plant size: to produce 100 000 tons/y of cellulose pulp (700 tons/d of wood)

Capital investment: $34 million

Feedstock cost: $7.5 million/y

Labor, materials, and chemicals: $14 million/y

Product value:
   Cellulose pulp @ $350/ton, $35 million/y
   Pentose syrup @ 8¢/lb, $7 million/y
   Lignin @ 15¢/lb, $15 million/y

plosion as a pretreatment for cellulose hydrolysis and has optimized the time and temperatures in a gun for batch explosion of wood chips. The cost is the same or less than the size reduction steps of other schemes proposed for wood hydrolysis; thus, pretreatment accomplishes a dual purpose. The choice between organic solvent pulping of wood and steam explosion will depend on the value of the products. For instance, paper pulp commands a relatively high price compared to glucose from hydrolyzing the cellulose, and this may justify the cost of solvent treatment.

The lignin from the Iotech process is very easily recovered by extraction with dilute alkali. If cellulose in the Iotech process can be tailored to uses that rival the value of paper pulp, this all-aqueous technology should be highly profitable. About 7% of the exploded wood goes to the production of cellulase enzymes. Cellulase broth is added directly to the rest of the wood to achieve better than 85% of the theoretical glucose yield from cellulose. Hemicellulose hydrolyzes readily during steam explosion and is washed

out as a solution to be evaporated to a syrup for feeding cattle (Figure 4). Solid residue from enzymatic hydrolysis is rich in lignin which can be recovered in quite pure form by extraction with dilute alkali, or the residue can be sold directly for adhesive applications such as binding of plywood or chipboard where some inert fillers are desirable in the resin.

Tests of the Iotech process at a 1000-L scale at the Gulf pilot plant in Kansas achieved about 90% of the theoretical yield of glucose from cellulose, and fermentation to ethanol performed well. Formulations of wood binders using the lignin have received favorable evaluations from potential customers. There is interest in building the first Iotech factory in New York state. Capital costs will be kept down and plant startup will be easier because the initial products will be syrups and lignin; the preparation of fermentation products such as ethanol is a project for the future.

Economics furnished by the Iotech Corporation are in Table 3 (9). The return on investment appears to be among the best of any of the processes

for making chemicals from biomass.

Another advance that will lower the cost of enzymes is in recycling. Of the dozen or so components of cellulase, several bind strongly to cellulose. These can be recovered easily from the hydrolysate by adsorption on cellulosic material that can be blended with the solids fed to hydrolysis. A fraction of the enzymes on the solid residue from hydrolysis can be desorbed by simple means (10), and the extract would supplement the fresh enzyme. Already there are indications that about 50% of the cellulase can be recycled, and the impact on costs will be dramatic. β-Glucosidase, a key component that splits cellobiose to glucose, is not very stable and cannot be recovered by any tricks based on adsorption on cellulose. However, low-cost β-glucosidase can be obtained by a separate fermentation.

Another possible product can be made from the leafy residue if trees are harvested while green. Protein content is about 23%, and similar material is sold in Europe as cattle feed. However, if entire trees are collected, soil fertility will decline quickly unless fertilizers are used.

Energy balances

Obviously, it makes no sense to make ethanol as a gasoline substitute if it takes as much or more petroleum to produce the ethanol. The energy expenditures for growing the crop, manufacturing the farm machinery, transporting the crop to the factory, constructing the factory, and conversion to fuels may exceed the energy content of the fuel. There are additional hidden costs, such as the energy to manufacture the fertilizer, to pump irrigation water, and the like. However, crop residues need not incur the energy penalties that were allocated to the valuable food portion. Less valuable tree species have little energy investment because the harvesting machinery is usually in place for the principal trees. Nevertheless, future plantations for biomass only must be energy-conscious. The ideal would be a multipurpose crop with food or fiber products of high value to defray costs.

There have already been energy-saving improvements in ethanol processes. For example, older distillation technology for ethanol took more heat energy than the heat of combustion of the product. Good engineering with heat exchangers and vapor recompression to power subsequent distillation stages can save two-thirds of the distillation energy; however, equip-

FIGURE 4
Steam explosion refining

Wood chips → Steam explosion → Washing → Liquid → Concentrate to pentose syrup

Washing → Enzymatic hydrolysis → Liquid → Concentrate to glucose syrup

Enzymatic hydrolysis → Solid → Lignin
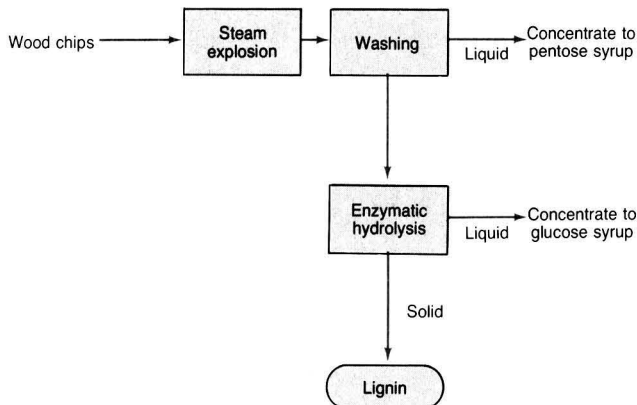
TABLE 3
Economics of biomass refining by steam explosion (9)

| | Projected production cost | |
	Syrup cost/ kg (dry)	Lignin cost/kg
Raw materials	$0.021	$0.046
Energy	.021	.026
Maintenance	.013	.015
Depreciation	.013	.015
Overhead	.009	.018
Direct labor	.003	.011
Apportioned unit cost	$0.080	$0.131
Probable selling price	$0.17/kg	$0.44/kg

Plant size: 1000 dry tons of wood/d
Plant cost: $70 million

ment costs would increase markedly. Spent warm streams can be used throughout the factory to economize on heat, but again, there are costs associated with heat exchangers and piping.

The distillation of ethanol–water solutions is quite efficient in the region of the liquid-vapor diagram where the lines are widely separated, but many distillation stages are needed as the lines come together. It may save appreciable energy to distill to about 85% ethanol and to use a drying scheme or a membrane process to reach almost absolute ethanol. Vapor-phase drying of ethanol reduces the energy for recovery to about 20% of the heat of combustion of the product ethanol (11). Another attractive option is to purify the ethanol partially by distillation and to add it to gasoline to produce gasohol directly.

In a developed nation with strong markets for organic chemicals, refining of biomass to valuable products could be highly profitable. Other countries may find it more expedient to burn biomass as an easily implemented substitution for imported oil. Gasification of biomass and anaerobic digestion to methane has inherent limitations which means that cheap feedstocks must be available and other special circumstances must be present in order to justify an investment. New digester designs may improve prospects for methane, and new designs for fermenters to aid biomass refining are also appearing.

The prospects are good that the private sector will commercialize processes for biomass fuels and chemicals with little need for government help. Nevertheless, government must be cooperative; it should realize that competing industries have many sorts of direct and indirect subsidies and give biomass a chance to compete fairly.

Additional reading

Periodic reports about projects supported by the U.S. Dept. of Energy have appeared in the *Alcohol Fuels Program Technical Review*, available from Larry Douglas, SERI, 1617 Cole Blvd., Golden, Colo. 80401.
Reviews can be found in Bungay, H. R. "Energy, the Biomass Options"; Wiley: New York, 1981; Bungay, H. R. *Adv. Biochem. Eng.* **1981**, *20*, 1; and Blanch, H. W.; Wilke, C. R. *Rev. Chem. Eng.* **1982**, *1*, 71.

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Continental-scale variations in precipitation chemistry

*Ion concentrations are dominated by land use
and proximity to man-made emissions*

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Precipitation chemistry has received considerable attention over the past several years, with much of that attention focusing on the acidity of rain and snow and on the associated environmental consequences of acid deposition (*1–5*). Gorham (*5*) and Barret and Brodin (*6*) performed early studies of acid precipitation in nonurban areas of England and Scandinavia far from industrial centers. Likens identified the magnitude and spread of acid precipitation in the northeastern U.S. (*7*); reports of acid precipitation throughout the world continue to appear in the literature (*4*).

Acid precipitation, due primarily to the presence of the strong acids H_2SO_4 and HNO_3, has been implicated in watershed acidification (*3, 8, 9*) and in the decline of fish populations in affected lakes (*3, 10, 11*). Terrestrial effects, including soil acidification, loss of fertility, interference with the nitrogen cycle, and groundwater acidification have been suggested (*1–3, 12–15*).

Rain-borne NH_4^+, Ca^{+2}, and Mg^{+2} are also of special interest because they act to neutralize acidity and also act as nutrients. Kilham has reported on the role acid precipitation may play in the alkalinity of some lakes (*16*). Lead in precipitation is derived to a large ex-

tent from gasoline combustion, while Zn and Cd are indicative of other anthropogenic activities (*17*). The toxicity of these and other metals increases the importance of obtaining adequate information about their distribution in precipitation.

The concentration of a particular element in precipitation is controlled by the strength of its source (either local emissions or long-range transport), the presence of sinks other than precipitation (for example, dry fallout or gaseous absorption), and precipitation-scavenging processes. Chemical concentrations in precipitation are high near large emission sources and where precipitation intensity is low. Conversely, low concentrations are indicative of a low supply of these elements (resulting from weak sources or additional sinks) or a large volume of precipitation diluting the components scavenged by the rain.

Investigations of precipitation chemistry on a continental scale can reveal where the regional sources and sinks for different elements are located. Historical trends are indicated by changes in concentrations that occur over a wide area between sampling periods. Similar changes observed at an individual sampling station would not be as definitive an indication of major changes in precipitation chemistry because local conditions could be responsible. Sediment stratigraphy and the accumulation of elements in soils and vegetation (especially mosses and lichens, which are often wholly dependent on the atmosphere for their nutrient supply) provide additional information about spatial and historical variations in precipitation chemistry, most notably when those data are

calibrated against precipitation chemistry (*18–20*).

Continental-scale studies

In 1955–56, Junge and co-workers investigated precipitation chemistry on a continental scale in the U.S. (*21–23*). One of their conclusions was that soil dust was a major source of ions in rain over continents. Marine aerosols near coastal areas are rapidly diluted in the continental air mass and become an insignificant source of ions in the precipitation farther inland. Studies covering the north-central U.S. carried out by Thornton and Eisenreich (*24*) and Munger (*25*) support this idea.

In 1966–67, the National Center for Atmospheric Research analyzed major ions and trace metals in precipitation using a 32-station network (*26, 27*). Anthropogenic activity was implicated as the primary source of Pb, Zn, Cu, Fe, Mn, and Ni. Lead was correlated with the amount of gasoline consumed in the vicinity of the collection stations. Since the late 1970s, the Canadian Network for Sampling Precipitation (CANSAP) and the U.S. National Atmospheric Deposition Program (NADP) have investigated precipitation chemistry across much of North America. The distribution of sites and preliminary data for the CANSAP, NADP, and MAP3S/RAINE precipitation networks can be found in References 28, 29, and 30, respectively.

Investigative methods

For this article, the concentrations of major ions and selected trace elements in precipitation were compiled from numerous regional and local precipitation studies and data collected

TABLE 1
Data sources of precipitation chemistry

Location	Time	Collector	Schedule	No. of sites	Reference
U.S. network	1976–80	wet-only	monthly	7	83, 84
NADP, U.S. network	1/79	wet-only	weekly	33	29
Adirondack region	4/78–8/79	wet-only	event	7	85
Florida	7/76–10/77	wet-only	event	1	86
Ontario	8/76–7/78	wet-only	variable	1	87, 88
Canadian network	11/77–12/79	wet-only	monthly	48	89
Minnesota	4/78–7/79	wet-only	event	3	24, 25
Los Angeles, Calif.	9/78–9/79	wet-only	event	9	69
Northeastern U.S.	1976–80	wet-only	event	8	30
Alberta	5/75–4/76	wet-only	event	1	90
Kentucky	1971–80	wet-only	—	1	TVA, unpublished
Lake Tahoe area, Nev.	10/77–9/78	wet-only	—	1	91
Central Minnesota	1977–78	wet-only	event	1	92
Lake Michigan	9/75–12/76	bulk	monthly	21	55, 56
Iowa	1971–73	bulk	weekly	6	93
North Dakota	1981	wet-only	event/monthly	2	51
Ontario	6/73–5/74	bulk	variable	4	94
New York	8/70–7/71	bulk	monthly	6	95
Washington	8/75–7/76	bulk	—	1	96
Manitoba–Ontario	1973–77	bulk	bimonthly	1	97
Florida	7/77–9/79	wet-only	event	1	98
Nebraska	1973	wet-only	event	1	99
Indiana	8/73–11/73	bulk	—	1	100
New Mexico	1976	snow	—	1	101
Michigan	9/72–12/74	bulk	—	3	102
Central Ontario	5/77–9/77	wet-only	variable	2	89
Minneapolis, Minn.	1978–79	wet-only	event	1	103
Tennessee	6/73–5/74	wet-only/bulk	monthly	1	104, 105
South central Ontario	1972–73	bulk	—	1	106
San Francisco, Calif.	12/74–4/75	bulk	—	1	75, 76
North Carolina	7/75–4/77	bulk	variable	1	107

at individual sites operated over the past 10 years. From these data, and the NADP, CANSAP, and MAP3S information, isopleths of the concentrations of major elements were constructed. In addition to providing insight into continental-scale patterns of precipitation chemistry, the geographical variations in atmospheric fluxes may be used to investigate metal and nutrient accumulation in ombrotrophic bogs throughout eastern North America (31).

From the data base was created a file of concentration values in precipitation at specific locations identified by longitude and latitude. Matrices of concentrations at regularly spaced coordinates corresponding to a 90° by 50° longitude–latitude grid were generated by interpolating from the original data file. The WORLD Projection and Mapping Program was used to construct concentration isopleths from the array of interpolated data (32). The contour lines and map outline were stored in a longitude-latitude coordinate system and projected onto an x–y plotter.

Ideally, the only data that should be compared are those for samples collected and analyzed by identical techniques. A variety of data sources, however, was used to generate a data base sufficiently large to make trends apparent and statistically significant. Most of the data were derived from wet-only precipitation samples collected on an event, weekly, or biweekly schedule, but some data were derived from bulk precipitation samples. The inclusion of dryfall in bulk samples yields higher concentrations of soil-derived elements and lower H^+ concentrations than those measured in wet-only precipitation (33, 34).

Analysis of variance indicates that the mean concentrations of K^+, NH_4^+, Mg^{+2}, Ca^{+2}, SO_4^{-2}, and NO_3^- in the bulk precipitation samples were significantly higher than in the wet-only samples ($p < 0.01$) for regions having exposed, calcareous soils. But the mean concentrations of Na^+, Cl^-, and H^+ were not significantly different for the two types of samples in coastal and forested areas and in regions where dustfall was not dominant. This distinction is not totally definitive because the sites for which bulk precipitation data were used were clustered; geographical differences in precipitation chemistry could be responsible for part of the observed differences between the two groups.

For the ions that showed significant differences between bulk and wet-only data, isopleths were generated with and without the bulk data. For SO_4^{-2},

NO$_3^-$, and NH$_4^+$, the differences between the two sets of isopleths were minor; without including bulk precipitation data, concentrations differed only around Iowa by ~10 μeq L^{-1}. However, maxima in Ca^{+2} and Mg^{+2} were evident only when the bulk precipitation data were included in the isopleths, and therefore wet-only data were used for these two ions.

The inclusion of some data for collection periods other than whole (or multiple) year(s) may be a source of bias because precipitation chemistry varies significantly from season to season. Different collection frequencies (event, weekly, monthly), sampler designs, and analytical procedures may also introduce biases in the data set. Inspecting the isopleths shows, however, that the computing routine is not strongly influenced by individual data that are in disagreement with regional data trends. Furthermore, the magnitude of the concentration trends observed is greater than could be credibly accounted for by sampling and analytical errors (35). The existence of large regions with generally uniform concentrations further supports the validity of these data.

One additional difficulty is that few data on precipitation chemistry were available for some regions of North America (Figure 1, Table 1). More data should be obtained for the Gulf Coast–Lower Mississippi valley and for the plains and Rocky Mountain states in the U.S. Lewis and Grant (36) and Lewis (37) recently published information on precipitation chemistry at Como Creek, Colo., and several new NADP sites have been established in some of these areas.

Results

The isopleth maps for Ca^{2+}, Mg^{2+}, and K$^+$ all show midcontinental concentration maxima centered over the northern prairies with decreasing concentrations towards the coasts

FIGURE 1
Distribution of precipitation sampling sites in North America used in constructing isopleths
▲ Bulk samplers;   ● wet-only samplers

FIGURE 2B
Average concentrations of Mg^{+2} in North American precipitation (μeq L^{-1})

FIGURE 2A
Average concentrations of Ca^{+2} in North American precipitation (μeq L^{-1})

FIGURE 2C
Average concentrations of K$^+$ in North American precipitation (μeq L^{-1})

FIGURE 3A
Average concentrations of Na⁺ in North American precipitation (μeq L⁻¹)

FIGURE 3B
Average concentrations of Cl⁻ in North American precipitation (μeq L⁻¹)

FIGURE 4
Average concentrations of NH₄⁺ in North American precipitation (μeq L⁻¹)

(Figures 2a–c). Calcium concentrations range from ~100 μeq L^{-1} in the prairies to ~10 μeq L^{-1} in the forested areas of the northeastern and far western U.S.

Variations in Mg^{2+} and K^+ concentrations mimic the Ca^{2+} behavior. Concentrations of Mg^{2+} range from 60 μeq L^{-1} in the prairies to 10 μeq L^{-1} in the Far West and Northeast. Concentrations of K^+ similarly range from 6–10 μeq L^{-1} to 1–3 μeq L^{-1} over these same geographical areas. As expected, major cation concentrations in precipitation are highest where agricultural activity exposes soils to wind erosion (24, 25). The relative abundances of Ca^{2+}, Mg^{2+}, and K^+ in rainfall closely follow the relative abundances of these cations in the soil (24, 38) and the earth's crust (39).

The concentration isopleths of both Na^+ and Cl^- exhibit opposite behavior with concentration maxima along the Pacific and Atlantic Ocean coasts and lower concentrations inland (Figures 3a, b). Sodium and Cl^- concentrations peak at ~40–60 μeq L^{-1} along the coasts and drop to ~10–20 μeq L^{-1} in the midcontinental region. The geographical variations of Na^+ and Cl^- concentrations clearly indicate that sea salt is the major contributor along the coasts. In general, the coastal areas receive precipitation with a Na^+:Cl^- mole ratio near 1:1, whereas ratios may vary from 3:1 to 1:3 in midcontinental areas with differing soil types, vegetation, and rainfall.

Maximum concentrations of NH_4^+ in precipitation are found over central North America (Figure 4); the region
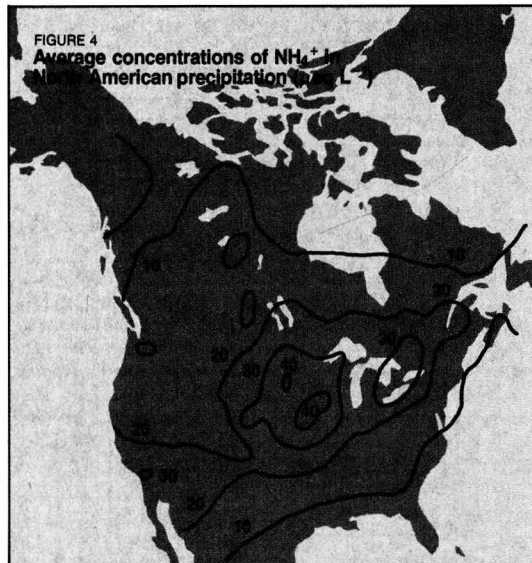
where NH_4^+ concentrations are greater than 20 μeq L^{-1} covers much of the upper Mississippi valley and Great Lakes. Ammonium ion concentrations vary seasonally and range from ~40 μeq L^{-1} in the upper Midwest to ~10 μeq L^{-1} near the coasts and in forested areas. The exception is the Los Angeles basin, which has anomalously high average NH_4^+ levels of ~30 μeq L^{-1}. Ammonium ion concentrations of 30–40 μeq L^{-1} are found in areas where agricultural production is heavy or there are numerous animal feedlots. Deciduous and coniferous forests apparently are

not major sources of atmospheric NH_3 or NH_4^+ in rainfall.

Maximum concentrations of SO_4^{2-} and NO_3^- are centered over the lower Great Lakes (Figures 5a, b) and to a lesser extent over the major urban-industrial centers of the northeastern U.S. Concentrations of NO_3^- are 30 μeq L^{-1} or greater over most of the Great Lakes basin and Ohio valley and parts of the upper Mississippi valley. The shape and spacing of the NO_3^- isopleths indicate that NO_3^- is somewhat uniformly distributed over the continent. This pattern may indicate that $NO_x(g)$ and $HNO_3(g)$ either

have many sources well dispersed over the continent, or have relatively long atmospheric residence times, or both. Nitrate concentrations range from ~50 μeq L^{-1} in the lower Great Lakes area to ~10 μeq L^{-1} in the southern U.S. and in the sparsely populated regions of northern Canada. Nitrate concentrations of 30 to 40 μeq L^{-1} in the Los Angeles basin result from numerous NO_x sources such as automobiles.

Sulfate concentrations exhibit a more variable pattern having several regional maxima (Ohio River valley–Lower Great Lakes; northeastern U.S.) typified by high concentrations and closely spaced isopleths. Concentrations of sulfate are highest on the Atlantic coast and generally decrease southward and westward with few exceptions. The SO_4^{2-} isopleth representing 60 μeq L^{-1} roughly corresponds to the 30 μeq L^{-1} NO_3^- isopleth. For the northeastern U.S. only, Pack generated SO_4^{2-} and NO_3^- concentration isopleths which show that maximum values are found in the lower Great Lakes basin (40). This is in agreement with the recent NADP (41) and MAP3S/RAINE (30) data. Our isopleths, which include additional data, are comparable but show a further extension westward and southward of high SO_4^{2-} and NO_3^- concentrations; they are supported by maxima in SO_4^{-2} and NO_3^- concentrations published by Wilson and Mohnen (41).

Hydrogen ion (H^+) concentrations in precipitation are at a maximum in the northeastern U.S., where they ap-proach 100 μeq L^{-1} (pH 4.00) (Figure 6). The 10 μeq L^{-1} isopleth (pH 5.00) encompasses nearly all of North America except for the northern plains and western Canada. This area is greater than indicated by most previously published isopleth maps for H^+ (42–46). All of the various H^+ isopleth maps agree that the H^+ maximum occurs over the northeastern U.S. and southern Ontario in Canada, in the prevailing downwind direction of major sources (41, 47, 48).

Data on trace-metal concentrations in precipitation are scarce. Most of them have been generated for sites in eastern North America, the northeastern and midwestern U.S., and adjoining areas of Canada (24, 49–51). We constructed isopleths of Fe, Zn, and Pb, which had the most extensive data base for eastern North America (cf. Figure 7a, b, c). Trace-element concentrations in precipitation have been recently summarized by Galloway et al. (49).

Lead concentrations reach 30 to 50 μg L^{-1} on a regional basis in the northeastern U.S. and at the eastern edge of the Great Lakes basin. Lead concentrations are also 30 μg L^{-1} or greater in a large part of the upper Mississippi River valley and in the Chicago, Ill.–Gary, Ind., areas. In the less populated areas to the south and north, lead concentrations decrease, although concentrations in the 20 μg L^{-1} range exist in the Sudbury, Ontario, region. This pattern corroborates the conclusion of Lazrus et al. that human activity such as gasoline combustion is the major source of Pb in precipitation (27). For comparison, median Pb concentrations are approximately 0.14, 15, and 49 μg L^{-1} in remote, rural, and urban areas, respectively (24, 49).

Maximum Zn concentrations, which may exceed 90–100 μg L^{-1}, are centered over the prairies and upper midwest. Zinc concentrations decrease to 10–30 μg L^{-1} to the south and east but remain high northward into Canada. This pattern suggests that most atmospheric Zn (aerosol or rain) is derived from wind-blown soil. There is little doubt, however, that Zn levels remain at anomalously high levels east and north of Lake Superior, possibly due to atmospheric emissions from smelting and mining operations. For comparison, median Zn concentrations in precipitation over remote, rural, and urban areas are 0.22, 45, and 40 μg L^{-1}, respectively (49). Zinc in urban precipitation is derived from soil, industrial, and automotive (i.e., tire wear) sources (52, 53).

Iron levels are highest where soil is exposed by agriculture and in regions north of the lower Great Lakes, peaking at 125 to 150 μg L^{-1}. Iron concentrations in forested areas of eastern North America range from 25 to 50 μg L^{-1}. The primary source of atmospheric Fe is wind-blown soil with additional contributions from Fe mining (northeastern Minnesota, Ontario, Canada) and urban/industrial complexes (Ohio valley–lower Great Lakes) (54). Continental background concentrations are ~25 to 50 μg L^{-1} in agricultural areas of the midcontinent.

FIGURE 5A
Average concentrations of SO_4^{-2} in North American precipitation (μeq L^{-1})

FIGURE 5B
Average concentrations of NO_3^- in North American precipitation (μeq L^{-1})

FIGURE 6
Average concentrations of H+ in North American precipitation (μeq L^{-1})

FIGURE 7B
Average concentrations of Zn in precipitation over the northeastern U.S. (μeq L^{-1})

FIGURE 7A
Average concentrations of Pb in precipitation over the northeastern U.S. (μeq L^{-1})

FIGURE 7C
Average concentrations of Fe in precipitation over the northeastern U.S. (μeq L^{-1})

The isopleths that have been presented for Pb, Zn, and Fe are preliminary because insufficient data exist for most areas. Many of the studies included in the data base were conducted at sites influenced by sources of anthropogenic metals. A network of background sites is required to construct a complete picture of the regional patterns of trace-metal concentrations and deposition. Furthermore, the sites where trace metals in precipitation have been studied are not well dispersed over the continent. Only around the Great Lakes have trace metals in precipitation been studied in

detail, and much of that data was not presented in a form that could be used for constructing concentration isopleths (24, 50, 55-57).

Discussion

Major cations and anions in precipitation may be separated into three important groups based on projected sources derived from isopleth maps shown here and in the literature: 1) Ca^{2+}, Mg^{2+}, K^+; 2) Na^+, Cl^-; and 3) SO_4^2, NO_3^-, NH_4^+, and H^+. The sources of these ions are wind-blown soil, dust, sea spray, and natural and anthropogenic emissions of precursor

gases and elements.

In their geographical distribution in the precipitation over North America Ca^{2+} and Mg^{2+} show a striking similarity ($r = 0.83$; $p \leq .001$) (Table 2), with K^+ exhibiting a similar trend. The western maxima coincide with the semiarid plains east of the Rocky Mountains. Because precipitation in this region averages less than 50 cm annually, it is likely to be more concentrated in soil components (58). Also, the flat, open landscape there and the tendency for salts such as lime and gypsum to accumulate near the surface in arid soils are conducive to

wind erosion of calcareous soil dusts (59). If adequate precipitation data were available for the southern plains, the isopleths of elevated Ca^{2+}, Mg^{2+}, and K^+ would probably extend farther south. Based on Ca^{2+} concentrations in excess of 100 $\mu eq\ L^{-1}$ for the mid-continental region, Junge and Werby (23) and Junge (60) conclude that soil is the major source of atmospheric Ca^{2+}, Mg^{2+}, and K^+. These conclusions have been supported by Rahn (61), Munger (25), and Thornton and Eisenreich (24).

The marine sea-spray influence on the distribution of Na^+ and Cl^- is evidenced by both their increased concentrations along the coasts (Figure 3) and the significant correlation between them (Table 2). The 20 $\mu eq\ L^{-1}$ isopleths for both Na^+ and Cl^- extend farther inland along the Pacific coast than the Atlantic coast, perhaps due to prevailing westerly winds and the accumulation of evaporated salts in the western deserts. Because few precipitation values were available for the Gulf and southern Atlantic coasts, Na^+ and Cl^- concentrations there are probably underestimated by the isopleths.

Emissions of gaseous precursors are significant sources of SO_4^{2-} (SO_2), NO_3^- (NO_x), and NH_4^+ (NH_3). Except for some particulate SO_4^{2-} from sea spray near the coast and SO_4^{2-} from soil dust in arid regions, most SO_4^{2-} in precipitation results from the oxidation of SO_2 and other reduced sulfur gases. For eastern North America anthropogenic emissions are about 90% of the total S emissions (47), and the highest total SO_2/NO_x emission density is located in the Midwest, the central Eastern Seaboard, and southern Ontario (62-64).

Photochemical reactions of nitrogen oxides give rise to NO_3^- aerosol and HNO_3 vapor. On a global scale, NO_x emissions from biological activity are 10-fold greater than anthropogenic NO_x emissions. But because U.S. emissions of anthropogenic NO_x are nearly 50% of the global anthropogenic total (65) and the biogenic emissions are distributed more evenly over the globe, the ratio of biogenic to anthropogenic NO_3^- is probably much lower in North America.

Over 99% of airborne ammonia is derived from natural biological processes (66), the most important of which is the decomposition of organic waste (60). A significant portion of the organic wastes, however, may be derived from human activity, particularly sewage disposal and agriculture. Anthropogenic emissions of NH_3 that may be important on a local scale include those from waste incineration, fossil fuel combustion, various industrial processes, and animal feedlots.

The dominant source regions for SO_2, NO_x, and NH_3 are suggested clearly by the isopleths for SO_4^{2-}, NO_3^-, and NH_4^+. Sulfate and NO_3^- concentrations are highest over the lower Great Lakes and Ohio valley. Sulfur dioxide emissions in the corridor from Indiana to Pennsylvania, where SO_4^{2-} concentrations are greatest, are 20 to 30 $g\ m^{-2}\ yr^{-1}$. These are the highest emissions anywhere in the U.S. (41, 67). The maximum NO_x emission density (15 $g\ m^{-2}\ yr^{-1}$) extends in a narrow corridor along the Atlantic coast from the Chesapeake Bay to Cape Cod (67). The NO_3^- concentration maximum may not occur there because increased annual precipitation may dilute concentrations. Emissions of NO_x are only slightly lower (10 to 15 $g\ m^{-2}\ yr^{-1}$) in the much larger region along the lower Great Lakes and Ohio valley where NO_3^- concentrations in precipitation reach a maximum. Note that SO_4^{2-} concentrations do not increase over coastal areas, suggesting that biogenic emissions of sulfur from shallow estuaries and marshes are not a major source of SO_4^{2-} in precipitation. A slight increase in emissions along the coast, however, could be offset by increased precipitation volume, and data on precipitation chemistry near the Gulf Coast is very meager.

The importance of agricultural activity as a source for NH_4^+ is indicated by the NH_4^+ maximum centered over the central U.S. The north-central U.S. underwent a change from prairie and timberland to agricultural land in the mid- to late 1800s, greatly increasing NH_3 fluxes from the soil and the NH_4^+ content in rain. The source of NH_4^+ is probably volatilization of NH_3 from extensive feedlots, or from fertilizer and manure applied to the soil in that region. The isopleths of NH_4^+ concentrations in precipitation agree with Lau and Charlson's (68) isopleths of NH_3 equilibrium partial pressures in the atmosphere and the NH_4^+ deposition mass of Wilson and Mohnen (41). The NH_4^+ isopleths also follow the NO_3^- and SO_4^{2-} isopleths over the Great Lakes basin and down the St. Lawrence River valley. This may be due partly to anthropogenic emissions of NH_3, but is more likely a result of the reaction of alkaline NH_3 with acidic SO_4^{2-} and NO_3^- aerosols; this aerosol mix forms the condensation nuclei for rain clouds over that region.

Junge has suggested that NH_4^+ in precipitation is due mostly to the volatilization of NH_3 from soils having pH values greater than 6.0 (22). Soil NH_3 production and soil pH determine NH_4^+ concentrations in areas where fertilizer applications are minimal and animal feedlots are absent.

Hydrogen ions in precipitation are derived almost entirely from homogeneous or heterogeneous oxidation reactions of SO_2 and NO_x to form H_2SO_4 and HNO_3 (9, 43). Protons generated by the oxidation of reduced S and N in emissions react with NH_3 and alkaline particles (e.g., $CaCO_3$, clays). The interaction between acid SO_4^{2-} and NO_3^- aerosols and NH_3 and alkaline dusts controls the concentration of free H^+. Thus, regions of the North American continent receiving large anthropogenic emissions of acid anions (that is, precursor gases) with correspondingly low neutralizing components have precipitation with the lowest pH. Likens et al. (43), Clark (48), Benkovitz (62), and Voldner et al. (63) recently reported the annual SO_2 and NO_x emissions in the eastern U.S. and southern Canada. The most acidic precipitation (i.e., lowest pH) occurs in and downwind of areas where the precursor emissions are greatest. The NH_4^+ (Figure 4) and major cation (Figure 2) isopleths clearly show that the eastern U.S. and southern Canada receive precipitation of low neutralizing capacity.

Electroneutrality demands that cations and anions be equal in precipitation. Unless other significant species are present or analytical errors are made, the following condition is met:

TABLE 2
Correlation coefficients for selected ion pairs in precipitation

Ion-ion association	r [a]
Ca^{2+}: Mg^{2+}	0.83
Ca^{2+}: K^+	0.65
Mg^{2+}: K^+	0.68
Na^+: Cl^-	0.62
Mg^{2+}: Cl^-	0.52
K^+: Cl^-	0.52
NH_4^+: SO_4^{2-}	0.61
NH_4^+: NO_3^-	0.73
SO_4^{2-}: NO_3^-	0.70

[a] Correlations significant at 0.001 level. Number of samples = 110–153

$$[Ca^{2+}] + [Mg^{+2}] + [Na^+] + [K^+]$$
$$= [HCO_3^-] + [Cl^-]$$
$$+ [NH_4^+] + [H^+] + [SO_4^{2-}] +$$
$$[NO_3^-]$$
$$\sum \text{cations} = \sum \text{anions}$$

For most regions of the country, cation/anion balances based on isopleth concentrations are between 0.90 and 1.10 (Table 3). In the prairies and in the San Francisco area, cation/anion balances differ from unity by 36% to 57%. Electroneutrality is achieved, however, when the HCO_3^- contributions estimated from pH, pCO_2, and cation values are included.

Based on precipitation chemistry and ion balances, the percentage of total acid anions neutralized by NH_4^+ and major cations was calculated for each part of the country. Ammonium ion in precipitation accounts for 13 to 35% of the total acid anion neutralized, and major cations represent 35% to 66%. Eight to 52% of the total acid anions are not neutralized; that is, they are balanced by H^+. Regions receiving precipitation of highest acidity, such as the northeastern U.S. and lower Great Lakes, have low NH_3 and low basic cation fluxes from the soil, resulting in low neutralizing capacity. In forested regions the precipitation has lower neutralizing capacity than in nonforested areas. Even in the Los Angeles basin where NO_x emissions are high, 75% of the total acidity is neutralized by basic cations (50%) and NH_4^+ (25%).

In most areas of North America, the SO_4^{2-} concentrations in wet-only precipitation are $\sim$ two to three times the NO_3^- concentrations. For example, in the northeastern U.S. and lower Great Lakes region where SO_4^{2-} concentrations are 80-100 μeq L^{-1} on a volume-weighted basis, NO_3^- concentrations are 40-50 μeq L^{-1}. Sulfate and NO_3^- concentrations are approximately equal in southern California, while SO_4^{2-}/NO_3^- ratios are 1.8-3.0 elsewhere. Although the acidity of precipitation has usually been associated with S emissions, Galloway and Likens present convincing evidence that recent increases in precipitation acidity are caused by disproportionate increases in NO_3^- (70). The NO_x emissions east of the Rocky Mountains are significantly greater than SO_2 emissions, but an unknown fraction of the atmospheric NO_3^- may be contributed by biologically induced soil emissions (48, 62).

Wet deposition

Wet deposition of major cations and anions was estimated for the geographical regions outlined in Figure 8 by multiplying concentrations determined from the isopleth maps by mean annual rainfall amounts for that area (Table 4). The concentration gradients of some ions are especially steep due to land use changes and variations in the amounts of precipitation. For these ions the deposition estimates reported should be viewed with some uncertainty even though they still provide regional rankings.

Precipitation fluxes of major cations east of the Rocky Mountains vary by a factor of only two (Table 4). Deposition of Ca^{2+}, Mg^{2+}, K^+, and NH_4^+ is greatest for the eastern edge of the prairies, where rainfall is $\sim$ 90 cm y^{-1}, but decrease to the west where rainfall drops to $\sim$ 40 cm y^{-1}. The upper and lower Great Lakes regions receive similar wet deposition of Ca^{2+}, Mg^{2+}, and NH_4^+, with fluxes of soil-derived constituents decreasing to the east. The highest flux of Na^+ and Cl^- is in the Pacific Northwest where high annual rainfall and proximity to the ocean coincide. With the exception of California, the overall flux of Na^+ and Cl^- is greatest in the coastal areas. Midcontinental areas receive as little as 10% of the sea salt flux in the Pacific Northwest. Junge attributes the lower Cl^- concentrations inland from the ocean to vertical tropospherical mixing as the marine air masses move inland (22).

Wet deposition of SO_4^{2-} and NO_3^- is highest in the northeastern U.S., Maritimes, and lower Great Lakes, achieving SO_4^{2-} fluxes of 60 to 70 meq m^{-2} y^{-1} and NO_3^- fluxes of 20 to 30 meq m^{-2} y^{-1}. The apparent high SO_4^{2-} flux in the Pacific Northwest may be representative only of the Seattle area and is not derived from marine SO_4^{2-}, which accounts for $\sim$ 10% of the 80 meq m^{-2} y^{-1} flux.

Almer et al. suggest that a SO_4^{-2} flux (wet) of $\sim$ 30 meq m^{-2} y^{-1} represents a threshold above which acid-sensitive watersheds will be impacted (71). There is general agreement that SO_4^{-2} wet deposition to acid-sensitive areas of 25-30 kg ha^{-1} y^{-1} will result in acidification of lakes (3, 9, 72) (2 meq m^{-2} y^{-1} is approximately equivalent to 1 kg ha^{-1} y^{-1}). Sulfate deposition in all areas east of the Mississippi River and throughout much of North America exceeds 30 meq m^{-2} y^{-1}. The acid-sensitive regions defined by Galloway and Cowling as pictured in Figure 8 (73) and later expanded (74) all receive SO_4^{2-} fluxes greater than the threshold value, although H^+ fluxes vary by an order of magnitude. Acid (H^+) fluxes of 40 to 70 meq m^{-2} y^{-1} have resulted in acidification of sensitive lakes, but other more subtle changes may occur at lower H^+ loadings. The Adirondacks, Nova Scotia, and eastern Ontario, where lake acidification has occurred, are within the region of highest H^+ loadings (43).

Because rainfall decreases and acid-neutralizing species increase to the west, H^+ loadings also decrease. Wet deposition of acidity in most of California is low because annual rainfall is low. McColl, however, has documented substantial H^+ concentrations and fluxes in the Sierra Mountains (75, 76). Highly acidic fog in the Los Angeles basin may generate acid fluxes not measured by rainfall collectors (77). (It should be remembered that the deposition of ammonium ion from the atmosphere is thought to release at least as much acid to the soil as an equivalent amount of H_2SO_4.)

TABLE 3

Ion balances and percent acid neutralized by NH_4^+ and basic cations

| Region | Σ^+/Σ^- | % Neutralized by | | |
		NH_4^+	$\Sigma Ca^{2+}, Mg^{2+},$ Na^+, K^+	Total
Northeastern U.S.	1.06	13	35	48
Maritimes	0.94	13	48	61
Lower Great Lakes	1.06	22	38	60
Upper Great Lakes	1.05	27	51	78
Southeast U.S.	1.02	20	42	62
Pacific Northwest	1.10	13	79	92
Los Angeles, Calif.	1.00	25	50	75
Western prairies[a]	1.57	30	66	96
Eastern prairies[a]	1.36	35	55	90
San Francisco, Calif.[a]	1.44	23	65	88

[a] $\Sigma^+/\Sigma^- \neq 1.0$ because HCO_3^- contribution was not included in study.

FIGURE 8
Regions with lakes that may be sensitive to acid inputs on the basis of bedrock geology[a]
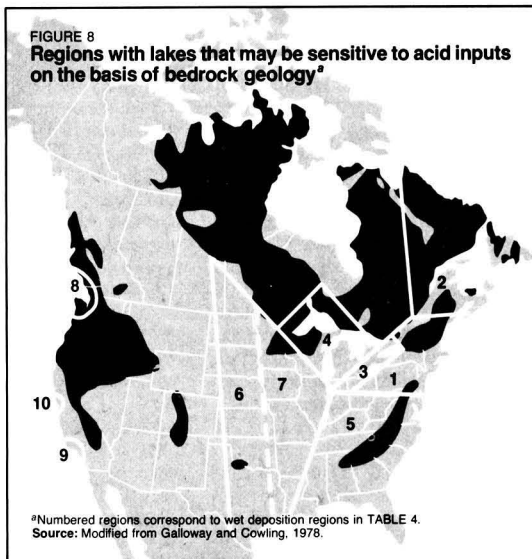
[a]Numbered regions correspond to wet deposition regions in TABLE 4.
Source: Modified from Galloway and Cowling, 1978.

TABLE 4
Wet deposition of major cations and anions

Region	H₂O (cm)	H⁺	Na⁺	K⁺	NH₄⁺	Ca²⁺	Mg²⁺	Cl⁻	NO₃⁻	SO₄⁼
					(meq m⁻² y⁻¹)					
1. Northeastern U.S.	100	70	20	2	15	15	5	25	30	65
2. Maritimes	100	40	30	3	15	20	5	30	20	70
3. Lower Great Lakes	80	48	8	1.6	24	24	8	12	32	64
4. Upper Great Lakes	70	21	8	1.4	21	21	8.5	7	21	49
5. Southeastern U.S.	130	39	20	1.3	20	13	6.5	20	26	52
6. Western prairies	40	2	6	0.6	14	16	8	4	8	18
7. Eastern prairies	90	9	13	1.4	32	27	9	9	18	40
8. Pacific Northwest	200	30	60	6	20	40	20	60	20	80
9. Los Angeles area	40	10	10	1.6	10	4	4	12	12	16
10. San Francisco area	60	6	21	1.2	12	6	6	12	12	12

The flux of Pb in precipitation appears to be greatest in the northeastern U.S. and to decrease in the Great Lakes basin and southeastern U.S. Estimated Pb fluxes in the Northeast of ~ 30 mg m⁻² y⁻¹ correlate well with Pb accumulation in a Massachusetts pine forest floor (78) and Adirondack lake sediments (79). Also, Pb accumulation in Great Lakes and Sudbury sediments can be accounted for by precipitation fluxes (55, 80, 81). The fluxes of other metals over large areas cannot be calculated until more field measurements are available.

Historical trends

Although there is some controversy about the validity of establishing historical trends based on older studies that may not have used sampling and analytical procedures identical to those of recent studies, there is a strong suggestion that concentrations of several ions in precipitation have increased since 1955 when Junge set up a continent-wide network of precipitation samplers. Based on 1955–56 data, Junge plotted a maximum NH₄⁺ isopleth of 16 μeq L⁻¹ over the north-central U.S. (roughly the Corn Belt) corresponding to a wet flux of 20–30 meq m⁻² y⁻¹ (22). During the years since Junge's study, U.S. production of NH₃, which is used predominantly as fertilizer, nearly tripled from 4.2 × 10⁶ t y⁻¹ in 1962 to 13.7 × 10⁶ t y⁻¹ in 1975 (66). Along with the increase in the use of nitrogen fertilizer, both the size and density of ani-

mal feedlots have increased, raising the volume of manures, which are a significant source of NH₃ to the atmosphere (68). The increased loading of nitrogen in agricultural soil has led to an increase in NH₄⁺ concentrations in precipitation.

Nitrate and SO₄²⁻ levels in precipitation also appear to have increased since 1955. Junge plotted a 16 μeq L⁻¹ isopleth for NO₃⁻ over Lakes Erie and Ontario, where current data show concentrations in excess of 40 μeq L⁻¹ (22). Sulfate was 60 μeq L⁻¹ in the same region during 1955–56 (23) and is now 90 μeq L⁻¹ or more. The extent of the 60 μeq L⁻¹ isopleth, which was Junge's maximum, has increased to cover a large part of eastern Canada and the northeastern U.S. This comparison is incomplete because Junge had no rain collection sites in Canada. Note that NO₃⁻ has increased relative to SO₄²⁻ as suggested by Galloway and Likens (70).

Emission rates for NO_x and SO₂, the precursors to NO₃⁻ and SO₄²⁻ in precipitation, have increased substantially over this period. Emissions of NO_x have doubled from 12.5 × 10⁶ t y⁻¹ in 1955 to 25 × 10⁶ t y⁻¹ in 1975, and SO₂ emissions increased from 23 × 10⁶ to 33 × 10⁶ t y⁻¹ (82). Furthermore, the use of tall stacks, which disperse plumes over a wider area, has grown in recent years. Junge does not present data on H⁺ in precipitation during the 1950s.

One could hypothesize that increases in SO₄²⁻ and NO₃⁻ concentrations in precipitation would have increased the H⁺ concentrations, but that concomittant increases in NH₄⁺ could have neutralized the added H⁺. However, comparisons between our isopleths and the reconstructed H⁺ isopleths of Cogbill and Likens suggest that H⁺ concentrations have increased (42). The recent acidification of precipitation in North America has been further documented by Likens and Butler (46). The concentrations of other major cations do not appear to differ appreciably from levels observed during the 1950s, and their present spatial patterns are similar to those observed previously.

Because Lazrus et al. presented their 1966 data on trace metals in precipitation as symbols representing ranges that bracket the average concentration at each site (27), it is difficult to detect any changes in regional trace-metal concentrations since that time. For the most part, present-day concentrations of Pb are comparable to 1966 concentrations; Zn may have decreased in local areas, but since

knowledge about the surroundings of any of the sites is insufficient, we cannot determine if there has been a change in Zn concentrations in precipitation.

Summary and conclusions

Available data on precipitation chemistry in North America have been assembled and used to generate isopleth maps of ion concentrations in precipitation. Despite some deficiencies in the data and problems with combining data from different sources, the resultant isopleths can be used to identify regional patterns of major ions in North American precipitation. The information on trace-metal concentrations is less complete.

The major conclusion of this paper is that precipitation chemistry is dominated by local and regional land use patterns and proximity to anthropogenic emissions. Acidity is highest in precipitation where emissions of precursor anthropogenic gases are highest *and* the concentrations of neutralizing soil components are lowest.

High concentrations in precipitation suggest that the semiarid plains east of the Rocky Mountains are a major source area for Ca^{2+}, Mg^{2+}, and K^+. Ammonium concentrations are highest over central North America and are derived from agricultural fertilizers, animal feedlots, and natural soil processes. Nitrate and sulfate maxima are clearly associated with the major urban–industrial area surrounding the Great Lakes and industrial northeastern U.S. Hydrogen ion concentrations in precipitation are high where the supply of alkaline minerals, NH_4^+, Ca^{2+}, and Mg^{2+}, to neutralize acidity is small relative to acidic NO_3^- and SO_4^{2-}.

Sea salt appears to be the predominant source of Na^+ and Cl^-. Isopleth maps of Fe, Zn, and Pb concentrations in the northeastern quarter of the U.S. were constructed, and they suggest that urban–industrial areas are a major source of atmospheric Pb; Zn and Fe are derived from the wind erosion of exposed soils as well as from industrial processes.

In the future, changes in the factors controlling the strength of these sources may alter regional precipitation. Changes in dust resuspension, either through different agricultural practices and erosion control measures or climate shifts, will affect Ca^{2+}, Mg^{2+}, and K^+ concentrations. Ammonium concentrations will be affected by major changes in livestock populations or fertilizer applications.

Any changes in concentrations of these alkaline substances would have a secondary effect on precipitation acidity. Acidity and concentrations of NO_3^- and SO_4^{2-} would be influenced by any change in NO_x and SO_2 emissions. Lead concentrations will likely decrease in the future as the use of leaded gasoline is reduced, but will be partially offset by increasing coal combustion.

The northern Atlantic coast and lower Great Lakes basin have the highest wet-deposition rates for H^+, NO_3^-, and SO_4^{2-}. Wet deposition of Ca^{2+}, Mg^{2+}, K^+, and HN_4^+ is high in parts of the prairies, but decreases in the more arid West despite high concentrations in precipitation. Because of heavy rainfall, the Pacific Northwest has large precipitation loadings of many elements.

The concentrations of NO_3^-, SO_4^{2-}, and NH_4^+ in precipitation appear to have increased over the last 25 years. The impact of this additional nitrogen on N-limited ecosystems should not be ignored.

For most of North America there is a sufficiently complete precipitation chemistry network to explain the distribution of major ions in precipitation but not necessarily historical trends. However, information about major ions in the Gulf Coast–lower Mississippi valley and the southern plains and Rocky Mountains is still incomplete. Even less is known about the trace-metal content of precipitation over much of North America.
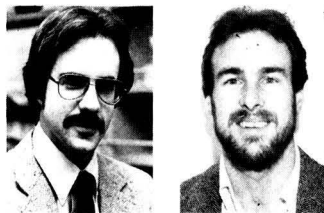
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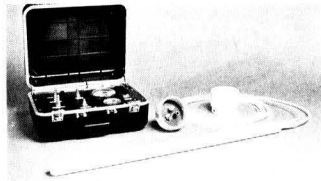
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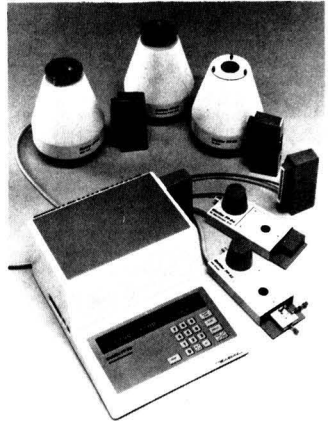
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Dual-channel, double-beam atomic absorption instrument is capable of determining almost any two elements simultaneously. It includes a CRT screen and an optional cell holder that allows it to function as an ultraviolet-visible spectrophotometer. A unique background correction system utilizes a hollow cathode lamp as its own background corrector. Instrumentation Laboratory **118**

Conductivity meter
Hand-held portable unit directly measures total dissolved solids in three ranges: 0.10 ppm, 0–100 ppm, and 0–1000 ppm. Samples are analyzed with ±5% accuracy in a built-in cup equipped with self-conditioning electrodes. The instrument automatically compensates for temperature and can analyze as little as 1.0 mL of liquid. Chemtrix **119**

UV–visible spectrophotometers
Microprocessor-controlled units use double-beam optics with holographically-ruled gratings and high-sensitivity photomultipliers that produce a spectral range from 195–900 nm. The sample compartment accommodates accessories such as flow-through cells and turrets. The digital interface gives the microprocessor control over the optics, all automated features, and displays. IBM Instruments **120**

Infrared thermometer
This unit has a linear output from 4–20 milliamp and a switch-selectable choice of 1 or 10 mV/degree. It contains an integral alarm and has a spectral range from 8–14 μm. E^{2}Technology **121**
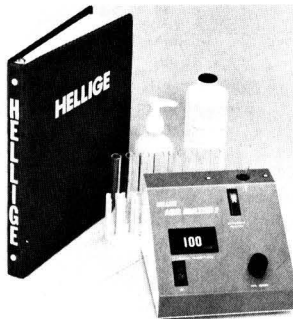
Water analysis system
Digital-reading spectrophotometer can be used for more than 65 water tests, many of which take less than one minute. The system includes a procedures manual that gives step-by-step instructions and allows testing by untrained personnel. Hellige **122**

Air chamber for balances
Ten-in.-high air chamber is designed to accommodate tall weighing containers and helps to eliminate the effects of air movement. This accessory is an option on all Arbor 1-mg and 0.1-mg balances and can be retrofitted in the field. Arbor Laboratories **124**

Digital thermometer
This is accurate to +0.1 °C over its range from −100 °C to 850 °C and has a resolution of 0.1 °C below 200 °C. It has a large 3 1/2 digit LCD display and uses a 9-V battery or an ac adapter for power. The probes are standard 100-ohm platinum RTD sensors and are configured for the measurement of liquids, gases, surfaces, and pierceable solids. Owen Instruments **125**

Analytical evaporator
Instrument prepares multiple test samples simultaneously for residue analysis. The rotating sample holder is attached to a spring hoist. The needle valve heights are adjustable to accommodate the mixed use of vials, test and centrifuge tubes, and Erlenmeyers. The bath temperature is thermostatically controlled below solvent boiling points from 35 °C to 70 °C. Organomation Associates **126**

Surface chemical analyzer
Analyzer combines scanning electron and scanning Auger microanalysis capabilities in one instrument. The important part of the instrument is a vertically mounted electron optical column that includes a large diameter cylindrical mirror electron energy analyzer and integral, coaxial electron gun. Most system functions are automated. Perkin-Elmer **127**

Activated carbon filters
These contain activated carbon impregnated on a variety of dust filtration substrates. They remove contaminants from air and liquid for residential, commercial, and industrial applications. Lewcott Chemicals and Plastics **128**

Toxicity analyzer
This screening tool determines the presence of toxic materials in a variety of samples ranging from rinse water to hazardous spills. It measures the influence of toxicants on the light output of a special strain of luminescent bacteria. Toxic materials decrease the amount of light emitted from these bacteria. From 5 to 15 min are required for each reading. Beckman Instruments **131**

ES&T
LITERATURE

Waste solidification. Papers explain how solidification helps to stabilize waste, clean up spillages, and perform similar tasks. Liners are also described. American Environmental Protection **151**

Toxic emission control. Bulletin 23-77 tells how granular activated carbon removes toxic and odorous emissions from air and lists gases so adsorbed. Calgon **152**

Chlorine dioxide. Brochure describes Oxychlor chlorine dioxide generating system for treating potable or process waters; trihalomethane effects are minimized. Dioxcide **153**

Dust extraction. Brochure describes Erasair dust extractor, which takes out up to 99.8% of total dust from air and 97.5% of respirable dust. Strobic Air **154**

Microprocessor capability. Literature tells how to add Datasette microprocessor capability to existing laboratory instruments. Gives data logging, processing, recording, and other capabilities; prices start under $1000. Precision Systems **155**

Calibration. Catalog lists equipment for calibration of measuring instruments, especially those that measure hydrogen sulfide. Catalog in English or Spanish. Houston Atlas **156**

Test chambers. Brochure lists a whole line of environmental test chambers with many different temperature/humidity conditions possible and three work space volumes. Tenney Engineering **157**

Safety management. Catalog lists products, books, and training programs in safety management. International Safety Academy **158**

Need more information about any items? If so, just circle the appropriate numbers on one of the reader service cards bound into this issue and mail in the card. No stamp is necessary.

Flow switches/meters. Catalog lists lines of flow switches for regulating flow and meters for measuring. Transamerica Delaval **159**

Disposal site liners. September issue of *Gundle Lining Review* tells why clay liners "may not be deserving of their positive and longstanding reputation." Gundle Lining Systems **160**

Hazardous wastes. Publication, *Rollins Report*, is addressed to those who manage hazardous wastes. October 1982 issue deals with problem of abandoned site cleanup. Rollins Environmental Services **161**

Leakage seal. Technical Bulletin TL-60 tells how a PVDF pump with a special seal solves leakage problems with corrosives and solvents. Vanton Pump & Equipment **162**

Venturi scrubbers. Brochure HS-MVS explains how venturi scrubber abates submicron particles and toxic gases from low flow rate streams. Heat Systems-Ultrasonics **163**

Biotechnology. Expanded catalog lists products and instruments used for biotechnology research. Featured is Fotosystem 1000 for scientific and laboratory documentation. FOTODYNE **164**

Analysis training. Catalog lists training programs in major fields of analytical, chemical, and clinical instrumentation. Savant **165**

Hazardous wastes:
Explaining the new EPA requirements

On Jan. 26, 1983, EPA regulations for the land treatment, storage, or disposal of hazardous wastes become effective. Required by the Resource Conservation and Recovery Act (RCRA) of 1976, these regulations, termed "interim final" standards, apply to owners and operators of new and existing facilities. The main emphasis of the regulations is protection of groundwater resources.

There are requirements for monitoring and corrective action. Engineers of the Michael Baker Corporation (Beaver, Pa.), have prepared so-called decision charts for these regulations. There is a decision chart, for example, for each of the three phases. These charts are available from the company.

Monitoring is divided into two types—*detection monitoring* and *compliance monitoring*. Detection monitoring is conducted to learn if contamination has migrated from a hazardous waste management site. If contamination is detected, then compliance monitoring must be implemented; its purpose is to identify the specific parameters of concern with respect to human health and the environment. At this point, it is necessary to determine if the concentration exceeds allowable levels or standards.

When a standard is violated, *corrective action* must be undertaken and continued until the contaminants are removed or treated in-place.

In 1981, Michael Baker Corporation expanded its waste management capabilities with the acquisition of Touhill, Shuckrow, and Associates. Its president, Dr. C. Joseph (Joe) Touhill, was a member of the *ES&T* advisory board in 1976–77. (See *ES&T*, January 1976, page 25–26.) Write direct: Michael Baker Corp., 4301 Dutch Ridge Rd., Beaver, Pa. 15009. Or phone David Hupe, 1-800-441-9014; in Pennsylvania 1-800-642-3790.

Pilot plant designs. Guide, "Glass Pilot Plants," features pilot plants for small production or research and development operations. Solid–liquid extraction, distilling, and many other operations covered O-I Schott Process Systems **166**

Computerized charts. Release announces line of computerized generation methods for charts, maps, diagrams, and other graphics. Texprint **167**

Spectrochemical equipment. Catalog lists spectrochemical equipment, accessories, and parts, as well as reference materials, sample preparation equipment, and other items. Baird **168**

Chromatographic bibliography. The company is offering free subscriptions to thin-layer and high-performance chromatography users. It is called *CAMAG Bibliography* and lists some scientific journal publications. Applied Analytical Industries **169**

Temperature monitoring. Brochure describes Series 7104 and 7106 monitoring panels for temperature. Digital thermometers are also listed. IMC Instruments **170**

Dust suppressant. Bulletin details Compound MR, a dust suppressant that can penetrate hydrophobic materials. Johnson-March **171**

Air pollution tracers. Brochure describes air pollution tracer studies for developers of power plants, mines, oil recovery operations, other industries. Featured is the CTA-1000 real-time gas analyzer. AeroVironment **172**

Analysis articles/items. *News & Notes for the Analyst* lists solutions to laboratory problems and features an article by Harvey Diehl on copper determinations. Hach **173**

Liner servicing. Brochure tells how Hercolor epichlorohydrin elastomers used in disposal site liners help avoid failures caused by ozone, weathering, and ultraviolet light. Hercules **174**

Water tracing. Bulletin 103 points out how fluorescein, a dye, can trace surface and groundwater movement. Turner Designs **175**

Laboratory facilities. Bulletin G-49 describes research and development laboratory facilities now available for outside contract work. Pyroprocessing is one offered. Fuller **176**

FBC coal combustion. Brochure explains dual-bed fluidized-bed combustion (FBC) technology for firing high-sulfur coal with little or no pollution. Steam output 20 000–120 000 lb/h; retrofit possible. Wormser Engineering **177**

Heater. Brochure describes high-temperature, energy-conserving heater for preventing fly ash cool-down and other uses. Bylin Heating Systems **178**

Tubular filters. Bulletin EF-14 lists a whole line of tubular filters, including fluorocarbon-lined ones. The Duriron Company **179**

Calibration instruments. TRANS-CATALOG describes and lists test, measurement, and calibration instruments for pH, conductivity, humidity, and many other parameters. TRANS-CAT **180**

Cooling tower fan drives. Catalog B-593 lists company's line of cooling tower fan drives. Mixing Equipment **181**

Laboratory plasticware. Catalog lists large line of laboratory plasticware for large and small labs. VWR Scientific **182**

FSOT capillary columns. Bulletin 48 lists line of stationary phases for fused silica open tubular (FSOT) capillary columns for analyzing various organic materials. Alltech Associates **183**

Acoustics. Paper E106-3016 details acoustic theory and explains how noise from various sources can be suppressed. Babcock & Wilcox **184**

Safety equipment. Catalog lists equipment, accessories, books, other items for safety in the workplace. Safety Management Inc. **185**

Emergency life support apparatus. Brochure details 5-min escape hood that can be entered to allow escape of smoke, fumes, and other hazards. International Safety Instruments **186**

Dew-point sampling. Application bulletin 3-052 discusses how a dew-point sampling system is designed and discusses hygroscopic properties of various materials. EG&G **187**

HPLC samples. Brochure explains how to prepare high performance liquid chromatography (HPLC) samples and solvents, and lists full line of filters and apparatus. Schleicher & Schuell **188**

Sewer technology. *Wastewater Technology*, a new publication, details new technology of pressure sewer systems, and explains how one application helped a community. Peabody Barnes **189**

Refrigerated circulators. Brochure PB-322B describes line of remote-controlled refrigerated liquid circulators. Temperatures 0–100 °C with control ±0.1 °C. Sybron/Brinkmann **190**

PCB field tests. Technical bulletin describers PCB field test kit that can cut analysis costs and provide an on-the-spot check in emergencies. Price is $2800. CENTEC **191**

Cascade impactors. Publication is a general instruction manual with comments and techniques for all sorts of cascade impactors. They are used for air sampling. BGI **192**

Pressure measurement. Brochure provides guide to selection of strain-gauge and LVDT-type pressure transducers and transmitters. Charts indicate available options. Schaevitz Engineering **193**

Nuclear data acquisition. Flier has highlights of a report concerning data acquisition necessary for nuclear plants to satisfy federal emergency instrument requirements. Ask about NSAC 51. Research Reports Center, Box 50490, Palo Alto, Calif. 94303 (write direct).

Irradiated foods. Booklet tells of a food preservation method using irradiation. Food *does not* become radioactive. American Council on Science and Health, 1995 Broadway, New York, N.Y. 10023 (write direct).

Reference materials. List shows standard reference materials and prices; a new standard offer is PCBs in oil. National Bureau of Standards, Washington, D.C. 20234 (write direct).

Companies interested in a listing in this department should send their releases directly to Environmental Science & Technology, *Attn: Literature, 1155 16th St., N.W., Washington, D.C. 20036*

ES&T
BOOKS

Solar Heat-N-Grow Window. Roger A. Moyer. 64 pages plus plans. Rodale Press Inc., 33 East Minor Street, Emmaus, Pa. 18049. 1982. $14.95, paper.

Being able to heat one's home with solar energy means that much less consumption of fossil fuels, along with attendant pollution reduction. This book provides instructions and plans for turning a window into a solar air heater, with a window greenhouse as an added bonus.

Photovoltaics, the Solar Electric Magazine. Mark C. Fitzgerald, Ed. Bimonthly periodical (to be increased to monthly). Fore Publishers, Inc., P.O. Box 3269, Scottsdale, Ariz. 85257. $24/y or $50 for 36 issues.

This magazine contains technical and nontechnical articles on technologies, products, and projects in photovoltaics and directly generated solar electricity. Each issue concentrates on a specific area.

Development without Destruction. Mostafa Kamal Tolba. ix + 197 pages. Tycooly International Publishing Ltd., 6 Crofton Terr., Dun Laoghaire, County Dublin, Ireland. 1982. $31, hardcover; $22, paperback; $12.50 for developing countries.

The author is the U.N. Environment Programme's Director-General. It includes speeches he made concerning population (at Bucharest), food (Rome), human habitat/settlement (Vancouver), desertification (Nairobi), and other topics of importance.

Making Pollution Prevention Pay. Donald Huisingh, Vicki Bailey, Eds. 168 pages. Pergamon Press, Maxwell House, Fairview Park, Elmsford, N.Y. 10523. 1982. $25.

This book stems from a conference sponsored by the Office of the Governor of North Carolina. It discusses work done by 3M Corporation, chemical recycling, systems approaches to waste management, how to turn pollution prevention into markets and profits, and cooperative efforts among various sectors of society.

Ground Water. H. M. Raghunath. 454 pages. John Wiley & Sons Inc., 605 Third Ave., New York, N.Y. 10016. 1982. $29.95, hardcover.

Groundwater is an extremely important source of water for man, and one under some threat. This book covers many aspects of groundwater, including assessment, utilization, and management. Procedures and designs for groundwater systems are presented, and rural water supply and irrigation use are emphasized. The book is aimed at graduate students and professionals.

Spirit of Enterprise: The 1981 Rolex Awards. Gregory B. Stone, Ed. xx + 460 pages. W. H. Freeman and Company, 660 Market St., San Francisco, Calif. 94104. 1982. Inquire as to price.

A Rolex Award, given by Montres Rolex S.A. (Geneva, Switzerland) consists of a gold chronometer and 50 000 Swiss francs. It is presented in three categories: applied sciences and invention, exploration and discovery, and the environment. This book explains in detail what the awardee did to earn his award. One example is a scheme for "banking" the genome of endangered species, awarded to a professor at the University of Tennessee.

Genetic Alchemy. Sheldon Krimsky. xiii + 445 pages. The MIT Press, 28 Carleton St., Cambridge, Mass. 02142. 1982. $24.95, hardcover.

This book examines the social history of the recombinant DNA controversy. It explains why concern over this field has arisen, why the public has become more involved, and what the science and policy debates are. "Worst-case" experiments, biological hazards, consensus positions, and guidelines are among the many topics discussed.

1982 National Conference on Environmental Engineering. Walter K. Johnson, Dennis R. Martensen, Eds. xii + 751 pages. American Society of Civil Engineers, 345 East 47th St., New York, N.Y. 10017. 1982. $56, paper.

The conference took place in Minneapolis in July 1981. Among subjects discussed there were policy, water supply and treatment, acid rain, waterborne diseases, hazardous waste, toxicity, and many other topics germane to environmental engineering and policy work.

Effects of Aerosols on Atmospheric Processes, NRCC No. 18473. 208 pages. Publications, NRCC/CRNC, Ottawa, Ontario, Canada K1A OR6. 1982. $8, paper.

This document deals with aerosols in the atmosphere. It covers particle emissions, characteristics, sources, optical properties in the atmosphere, effects on clouds, fog, precipitation, and atmospheric electricity, and effects on climate.

Winning the Games Scientists Play. Carl J. Sindermann. xii + 290 pages. Plenum Press, 233 Spring St., New York, N.Y. 10016. 1982. $15.95, hardcover.

This book offers some hints to aspiring scientists. For example, it tells how to use conferences to personal advantage, how to write articles successfully, and how to present them to journals and conferences. It offers detailed advice on dealing with bureaucrats, lawyers, politicians, and industry, as well as advice on handling interpersonal relationships.

Energy and Environmental Chemistry. Vol. 1, "Fossil Fuels"; Vol. 2, "Acid Rain." Lawrence H. Keith, Ed. Vol. 1, xiv + 450 pages; Vol. 2, xiv + 304 pages. Ann Arbor Science Publishers, Inc., 10 Tower Office Park, Woburn, Mass. 01801. 1982. $37.50, each volume, hardcover.

Volume 1 looks into the impact of tar sands and oil shale, oil spillages at sea, fugitive hydrocarbon emissions, and Lurgi coal gasification. Volume 2 discusses point source effects, regional effects, and theoretical considerations with respect to acid rain.

Carbon Dioxide Review 1982. William C. Clark, Ed. xix + 469 pages. Oxford University Press, 200 Madison Ave., New York, N.Y. 10016. 1982. $35, hardcover.

Carbon dioxide increases in the air may herald climatic changes to come. Here is a review that looks into such possible climatic changes, effects on minor atmospheric constituents, vegetation, measurements, and historical data.

Profit from Pollution Prevention. Monica E. Campbell, William M. Glenn. 404 pages. Firefly Books, 3520 Pharmacy Ave., Unit 1-C, Scarborough, Ontario M1W 2T8, Canada. 1982. $25, paper.

For $400 000, an electroplating company was able to recycle 90% of its rinse water and 99% of its chromium, copper, and nickel ions, and produce only 2% of the sludge it produced previously. This is one item in a book aimed at showing how such alternatives can "prevent a toxic tomorrow," and how waste recovery, when studied, can be shown to have surprisingly high profit or savings potential.

The Natural Geochemistry of Our Environment. David H. Speidel, Allen F. Agnew. xv + 214 pages. Westview Press, 5500 Central Ave., Boulder, Colo. 80301. 1982. $25, hardcover.

This book examines in detail the many materials that constitute the natural environment, including water, transport and sorption, soils and their composition, the oceans, and geochemical cycles and fluxes. Water flux is said to account for about 98% of the movement of chemical elements from one earth reservoir to another, the remaining amount being carried by air.

Management of Industrial Wastewater in Developing Nations. David Stuckey, Ahmed Hamza, Eds. x + 500 pages. Pergamon Press, Inc., Maxwell House, Fairview Park, Elmsford, N.Y. 10523. 1982. $70, hardcover.

This collection of papers includes diverse topics, among them the effect of pollution on relations between nations, the São Paulo (Brazil) wastewater pollution control project, surveillance and monitoring, anaerobic treatment, and wastes from specific types of industrial plants in the developing world.

Cleaning Up Coal: A Study of Coal Cleaning and the Use of Cleaned Coal. Cynthia A. Hutton, et al., Eds. xiii + 398 pages. Ballinger Publishing Co.,

54 Church St., Cambridge, Mass. 02138. 1982. $37.50, hardcover.

This book was prepared by INFORM, Inc. (New York, N.Y.). It examines coal-cleaning technologies, firms in the coal-cleaning business, advanced physical processes, and research and development organizations. Utilities owning coal-cleaning operations and those burning purchased, cleaned coal are also listed and described.

Herbicides and Plant Growth Regulators. W. W. Fletcher, R. C. Kirkwood. 408 pages. Methuen, Inc., 733 Third Ave., New York, N.Y. 10017. 1982. $49.95, hardcover.

This book reviews the history of herbicide development and use, benefits of herbicides, and benefits of chemicals used to regulate plant growth and production.

The Chemistry of Organophosphorus Pesticides. 2nd revised ed. C. Fest, K.-J. Schmidt. x + 360 pages. Springer-Verlag New York, Inc., 175 Fifth Ave., New York, N.Y. 10010. 1982. $78, hardcover.

Many organophosphorus pesticides are in use now; many are potent, even dangerous if used by improperly trained people. An advantage is that many are degradable. This book discusses their chemistry, biochemistry, modes of action, and metabolism by target pests and other organisms. A list of trade names and first-aid instructions are also given.

Nukespeak: Nuclear Language, Visions, and Mindset. Stephen Hilgartner, et al. xiv + 282 pages. Sierra Club Books, 2034 Fillmore St., San Francisco, Calif. 94115. 1982. $14.95, hardcover.

This book charges that the nuclear industry is covering up damaging information and says that nuclear proponents often confuse hopes with reality. Chapters discuss the "Atoms for Peace" program, secrecy, public relations, leaks, unaccounted-for materials, and many other topics.

Environmental Science Methods. Robin Haynes, Ed. x + 404 pages. Methuen, Inc., 733 Third Ave., New York, N.Y. 10017. 1982. $19.95, paper; $39.95, hardcover.

This book discusses various quantitative methods in the environmental sciences. Among topics covered are mathematics and statistics, measurement, computing, surveying, microscopy, remote sensing, social surveys, and laboratory techniques.

ES&T
MEETINGS

Feb. 3 Tallahassee, Fla.
1983 Florida Wastewater Management Seminar. The Florida Department of Environmental Regulation
Fee: $10.00. *Write:* Don Schiesswohl, Bureau of Environmental Regulation, 2600 Blair Stone Rd., Tallahassee, Fla. 32301; (904) 488-2582

Feb. 21–24 La Jolla, Calif.
Committee F-20 on Spill Control Systems. American Society of Testing and Materials
Write: Earl Sullivan, ASTM, 1916 Race St., Philadelphia, Pa. 19103; (215) 299-5514

Feb. 28–March 2 Washington, D.C.
10th Annual Energy Technology Conference and Exposition. American Gas Association and others
Write: Government Institutes, Inc., P.O. Box 1096, Rockville, Md. 20850; (301) 251-9250

Feb. 28–March 3 San Antonio, Tex.
1983 Oil Spill Conference. EPA, American Petroleum Institute, and U.S. Coast Guard
Fee: $200. *Write:* 1983 Oil Spill Conference, Suite 700, 1629 K St., N.W., Washington, D.C. 20006; (202) 296-7262

Feb. 28–March 4 Nashville, Tenn.
Development of Design Criteria for Wastewater Treatment Processes. Vanderbilt University
Fee: $725. *Write:* K. Ann Hood, Continuing Engineering Education, Vanderbilt University, Box 1525, Sta B, Nashville, Tenn. 37235; (615) 322-2924

March 3–4 Washington, D.C.
March 22–23 Houston, Tex.
The Fundamentals of Groundwater Quality Protection. American Ecology Services, Inc., and Geraghty & Miller Inc.
Write: Richard M. Miller, President, American Ecology Services, Inc., 127 East 59th St., New York, N.Y. 10022; (212) 371-1620

March 8–9 Nashville, Tenn.
May 18–19 Philadelphia, Pa.
Waste Incineration. Vanderbilt University

Fee: $475. *Write:* K. Ann Hood, Continuing Engineering Education, Vanderbilt University, Box 1525, Sta B, Nashville, Tenn. 37235; (615) 322-2924

March 28–30 Columbus, Ohio
3rd Ohio Environmental Engineering Conference. Ohio State University and others
Write: Harry G. Bhatt, Malcolm Pirnie, Inc., 6161 Busch Blvd., Columbus, Ohio 43229; (614) 888-4953

April 17–19 Milwaukee, Wis.
7th Symposium on Aquatic Toxicology. ASTM Committee E-47
Write: M. B. Cooper, ASTM, 1916 Race St., Philadelphia, Pa. 19103; (215) 299-5470

June 13–15 Ithaca, N.Y.
International Symposium on Gas Transfer at Water Surfaces. American Chemical Society and others
Write: W. H. Brutsaert, School of Civil and Environmental Engineering, Cornell University, Ithaca, N.Y. 14853; (607) 256-3676

Aug. 17–24 Estes Park, Colo.
International Humic Substances Society Meeting. USDA, Soil Conservation Service, U.S. EPA, USGS, and International Humic Substances Society
Write: Ronald L. Malcolm, U.S. Geological Survey, Box 25046, MS 407, Denver, Colo. 80225; (303) 234-3975

COURSES

Feb. 1–2 Los Angeles, Calif.
Feb. 9–10 Seattle, Wash.
Sample Preparation for Trace Inorganic Analysis. Finnigan MAT Institute
Fee: $300. *Write:* Nancy Kranpitz, Registrar, Finnigan MAT Institute, 11 Triangle Park Dr., Cincinnati, Ohio 45246; (513) 772-5500

March 28–April 1 Boston, Mass.
Fundamentals of Industrial Hygiene. Office of Continuing Education, Harvard School of Public Health
Fee: $800. *Write:* Office of Continuing Education, Harvard School of Public Health, 677 Huntington Ave., Boston, Mass. 02115-9957; (617) 732-1171

March 28–April 1 Boston, Mass.
Occupational and Environmental Radiation Protection. Office of Continuing Education, Harvard School of Public Health
Fee: $800. *Write:* Office of Continuing Education, Harvard School of Public Health, 677 Huntington Ave., Boston, Mass. 02115-9957; (617) 732-1171

March 30–April 1 Boston, Mass.
Risk Analysis in Environmental Health. Office of Continuing Education, Harvard School of Public Health
Fee: $500. *Write:* Office of Continuing Education, Harvard School of Public Health, 677 Huntington Ave., Boston, Mass. 02115-9957; (617) 732-1171

CALL FOR PAPERS

January deadline
Environmental Regulations and Their Impact on the Pharmaceutical Industry. American Institute of Chemical Engineers
The session will be held at the AIChE Summer National Meeting, Aug. 28–31, 1983, in Denver, Colo. *Write:* Charles V. Flemming, Schering Corp., 1011 Morris Ave., Union, N.J. 07083; (201) 558-5444

February 1 deadline
New Environmental Control Techniques from Mineral Processing Industries. American Institute of Chemical Engineers
The sessions will be held at the 1983 National Meeting of the AIChE, Aug. 28–31, 1983, in Denver, Colo. *Write:* Dr. Donald A. Dahlstrom, Eimco Process Equipment Co., P.O. Box 300, Salt Lake City, Utah 84110

February 1 deadline
4th International Conference on Heavy Metals in the Environment. Commission of the European Communities, National Research Council of Canada, and others
The conference will be held Sept. 6–9 at the University of Heidelberg, FRG. *Write:* Heavy Metals Secretariat, CEP Consultants Ltd., 26 Albany St., Edinburgh EH1 3QH, U.K.

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Sunlight-Induced Mortality of Viruses and *Escherichia coli* in Coastal Seawater

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■ The potential of sunlight for lethality toward enteric microorganisms was examined with use of pure cultures of *Escherichia coli* and three bacteriophages (MS2, ϕx-174, and T7) suspended in filtered coastal seawater. At temperatures that are common in temperate coastal waters, in vitro microbial mortality in sunlit seawater was significantly greater than that in seawater kept in the dark. *Escherichia coli* populations in sunlit seawater exhibited convex semilogarithmic mortality curves, suggesting that sunlight-induced death of *Escherichia coli* resulted from cumulative photochemical damage. Sunlight lethal for bacteriophage MS2 and *Escherichia coli* was not blocked by a polyacrylic filter, which exhibited a transmission cutoff at 370 nm. Under identical conditions of ambient sunlight exposure, *Escherichia coli* populations died more rapidly than populations of the single-stranded, RNA-containing bacteriophage MS2.

The prevention and control of microbial contamination of surface waters have been important concerns of environmental engineers for most of this century. In the past, relevant research has emphasized the bacterium *Escherichia coli*, because of its association with feces, and the coliform group, because of its use as a pathogen indicator. Recent research has focused on solar radiation (1–4) and protozoan predators (5–7) as the agents principally responsible for bringing about the decline of coliform populations that enter surface water bodies. Research directed toward understanding the behavior and fate of enteric viruses in the aquatic environment is fairly recent (8–13), so that there is presently little agreement on the principal mechanisms and prevailing rates of virus inactivation in surface waters (14, 15).

Interestingly, there have been no published studies that directly compare the survival of coliform bacteria and viruses under identical conditions in surface water (15, 16). This is curious since the efficacy of *E. coli* as a sanitary indicator organism depends in part on its being at least as resistant as enteric pathogens to lethal agents in the aquatic environment (17).

We examined solar radiation as a factor in the survival of three viruses and *E. coli* in oxygenated coastal seawater. Bacteriophages MS2, T7, and ϕx-174 were chosen for these experiments, because their nucleic acid content is similar

to that of the Picornaviridae, Adenoviridae, and Parvoviridae, respectively (16). In this report, we demonstrate that exposure to ambient sunlight can cause rapid mortality of these organisms in vitro, and we argue that availability of solar radiation is an important determinant of microbial mortality rates in coastal waters. In particular, we observed that (i) dieoff rates of sunlight-exposed *Escherichia coli* and the three bacteriophages were more than 10-fold higher than those of organisms kept in the dark and (ii) solar longwave radiation ($\lambda > 370$ nm) contributed to this lethality. Additionally, it was found that mortality of *Escherichia coli* was significantly greater than that of bacteriophage MS2 under identical conditions of ambient sunlight exposure.

Experimental Section

Bacteriophage Preparation and Enumeration. Bacteriophages MS 2 (ATCC 15597B), ϕx-174 (ATCC 13706B), and T7 (ATCC 11303B7) were purchased from the American Type Culture Collection (Rockville, MD) and were cultured by infecting exponential-phase host cells at room temperature in ECM broth. ECM medium consisted of an autoclaved basal broth of 10 g of tryptone, 8 g of NaCl, and 1 g of yeast extract per liter of glass-distilled, deionized water, to which were added 10 mL of filter-sterilized glucose solution (100 g L^{-1}), 2 mL of autoclaved 1 M CaCl$_2$·2H$_2$O, and 1 mL of filter-sterilized thiamine HCl solution (10 g L^{-1}). Purified bacteriophage cultures were obtained from 6–20-h crude lysates by the two-phase separation method (18). These cultures were diluted 10-fold in sterile 10 mM KCl and were filtered (0.22 μm) to make bacteria-free, stock phage suspensions, which were stored at 10 °C in screw-capped tubes. Phage titers were determined by the standard double-layer technique (19) by using a bottom layer of ECM medium with 15 g L^{-1} agar and a soft agar overlay of ECM medium without glucose or thiamine. Plaques were counted after 12–24 h of incubation at 37 °C.

Bacteria Preparation and Enumeration. *Escherichia coli* was initially isolated from an eosin–methylene blue–agar plate that had been directly inoculated with human feces and was maintained on agar slants made with brain heart infusion broth. Gram stain and oxidase reactions, morphology, and the API 20E diagnostic system (Analytab Products, Inc., Plainview, NY) were used to identify the isolate as *Escherichia coli*. Cell suspensions for survival trials were exponential-phase cultures grown in minimal glucose broth. Minimal glucose broth was

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made by adding 2 mL of filter-sterilized glucose solution (100 g L^{-1}) to 200 mL of an autoclaved mineral salts broth, consisting of 1.0 g of NH$_4$Cl, 6.0 g of Na$_2$HPO$_4$, 3.0 g of KH$_2$PO$_4$, 0.2 g of MgSO$_4$·7H$_2$O, and 0.5 g of NaCl per liter of glass-distilled, deionized water. Coliforms were enumerated by the spread-plate method by employing a medium of 5 g of lactose, 8 g of nutrient broth, and 15 g of agar per liter of glass-distilled, deionized water.

Survival Experiments. Seawater was obtained from a coastal site at Nahant, MA, and was filtered in the laboratory by using a 0.1-μm Nuclepore filter (Nuclepore Corp., Pleasanton, CA) within 8 h of sampling. Filtered seawater was stored at 5–10 °C in sterile, 2-L screw-capped flasks until use. Salinity of the coastal seawaters in these experiments ranged from 21 to 26 g kg^{-1} (S-C-T meter Model 33, Yellow Springs Instruments Company, Yellow Springs, OH).

For each survival test, a sample of filtered seawater was poured into a sterile flask and was brought to experimental temperature by submerging the flask in a constant-temperature water bath overnight. For light-exposure trials, approximately 350 mL of acclimated seawater was poured into a sterile 400-mL beaker. For dark survival trials, approximately 300 mL of seawater was poured into an aluminum-foil-covered, sterile 400-mL beaker or 500-mL screw-capped flask. An additional 300 mL of seawater was added to a BOD bottle, which was capped and refrigerated, for subsequent analysis of dissolved oxygen (20). This last step served to verify that the seawater suspensions were oxygenated at the start of each experiment.

For *Escherichia coli* survival tests, cultures in minimal glucose broth were diluted 10-fold in autoclaved, filtered seawater, and from 0.1 to 5.0 mL of the diluted culture was added to the appropriate seawater sample. For bacteriophage survival tests, phage stocks were diluted from 10^{-1} to 10^{-4} in autoclaved, filtered seawater, and from 2.0 to 5.0 mL of the diluted suspension was added to the appropriate seawater sample. In both cases, the seawater suspension was well mixed with a sterile pipette and then sampled to obtain initial concentration estimates. The range of initial concentrations was 10^3–10^5 colony-forming units/mL (CFU mL^{-1}) for *Escherichia coli* and 10^2–10^4 plaque-forming units/mL (PFU mL^{-1}) for the bacteriophages. In paired light–dark survival experiments, equal volumes of a microbial culture were used to inoculate a flask and/or a beaker(s) that contained different volumes of seawater; consequently, the initial concentration was slightly higher for the dark condition.

Inoculated beakers were then placed in a temperature-regulated water bath on the rooftop of our laboratory. Inoculated flasks were placed in a temperature-regulated water bath located either on the rooftop or in the laboratory. Periodically, the seawater in the flasks and beakers was mixed well with a sterile pipette and sampled for subsequent enumeration of viable organisms. For sunlight-exposure trials, 4–18 samples were taken for up to a 6-h period. For dark-exposure trials, sampling was completed from 15 to 51 times for up to a 6-week period. For most sampling times, multiple dilution series were completed. All decimal dilutions were made in 1.0 mM phosphate buffer (pH 7) with 0.1% proteose peptone added; recent reports attest to the value of organic additives to diluent media in the recovery of injured bacteria (21). Each tabulated concentration estimate was an arithmetic average of the colony counts from duplicate agar plates that had been inoculated from one decimal dilution series. Analysis of variance, using log-transformed plate counts, was employed to determine whether microbial
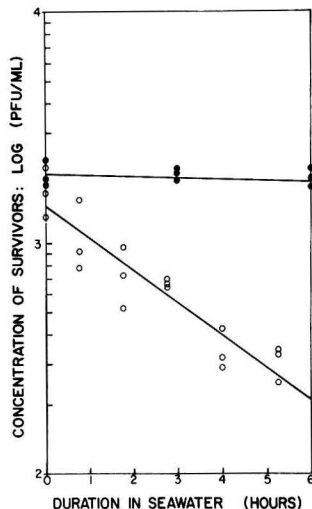
Figure 1. Effect of solar radiation on the survival of bacteriophage MS2 in filtered coastal seawater at 10 °C. Each data point is an independent concentration estimate of viruses exposed to sunlight on 7/9/80 (O) or kept in the dark (●).

populations experienced a significant (α = 0.05%, one-tail test) decrease after suspension in seawater (22). Exponential decay rates were calculated for each survival experiment by using the least-squares method of curve fitting and a linear model with log-transformed concentrations (23). Most survival experiments were terminated only after a 10-fold, or greater, reduction in concentration was observed. Solar radiation intensity was not measured during the sunlight-exposure trials, which were initiated between 1000 and 1200h in each instance.

For the survival experiments discussed here, the water bath temperature was set at 10–23 °C. For dark survival tests, the seawater temperature was generally no more than 1 °C higher than that of the bath. For sunlight-exposure experiments, the seawater temperature was as much as 3 °C higher than that of the bath.

Photoreactivation. In one set of experiments, we tested the hypothesis that *E. coli* and bacteriophage MS2 populations exposed to solar radiation could be photoreactivated (24) by a posttreatment exposure to white light. Quadruplicate plates were inoculated for each serial dilution during survival experiments at 10 °C. Half of these replicate plates were incubated in the dark without delay, as in all other experiments; these served as controls. Prior to incubation, the remaining sets of replicate plates received a 20-min illumination with a 500-W photoflood lamp (no. 2 Superflood EBV, GTE Sylvania, Danvers, MA). The phototreatment so provided (16) was found to maximize reactivation of far-UV-induced lesions (25). This posttreatment with white light did not increase viable plate counts of *E. coli* or bacteriophage MS2 that had been previously exposed to sunlit seawater (16). Consequently, inoculated plates did not receive this phototreatment in subsequent survival experiments. Our results are consistent with evidence (26) that shows that the photoreactivating enzyme can be destroyed by exposure to 365-nm radiation, which is present in sunlight.

Results

The effect of solar radiation on the persistence of the single-stranded RNA-phage MS2 in filtered seawater is shown in Figure 1 for a typical trial. Plaque counts (PFU

Table I. Exponential Inactivation Rates for Three Bacteriophages Suspended in Filtered Coastal Seawater

| | | | K_e,[a] h^{-1} | |
phage	temp, °C	date	sunlight-exposed populations	dark/control
MS2	10	7/9/80	0.32 ± 0.10	0.006 ± 0.002
	15	8/15/79	0.47 ± 0.24	0.005 ± 0.002
	15	8/16/79	0.41 ± 0.09	0.020 ± 0.002
	23	7/24/79	0.24 ± 0.14	0.027 ± 0.007
ϕx-174	15	8/15/79	0.65 ± 0.32	0.009 ± 0.002
T7	15	8/15/79	0.64 ± 0.19	0.006 ± 0.002

[a] Reported is the exponential inactivation rate (K_e) and half of its 95% confidence interval. The inactivation rate is the slope of the linear semilogarithmic survival curve, as estimated by using the least-squares criterion. For these experiments, the decimal reduction time (T90) is related to K_e as follows:

$$T90 = (\ln 10)/K_e$$

The salinity of the seawater was 26 g kg^{-1} for all experiments except one; it was 21 g kg^{-1} for the phage MS2 survival experiment at 10 °C.

mL^{-1}) with ECM agar are plotted on the logarithmic ordinate vs. duration of exposure in seawater. Clearly, bacteriophage MS2 at 10 °C is more stable in the dark than with sunlight exposure. Analysis of variance, using log-transformed plaque counts, revealed significant inactivation of the sunlight-exposed population ($N = 18$ concentration estimates) but not for the population kept in the dark ($N = 9$). Similar survival experiments with the single-stranded DNA-phage ϕx-174 and the double-stranded DNA-phage T7 demonstrated that these viruses are also inactivated rapidly in seawater upon exposure to ambient sunlight; decimal reduction times (T90) for phage populations exposed to sunlight ranged from 2.4 to 9.5 h (16).

Standardized residual analysis (23) gave us no reason to believe that the semilogarithmic dieoff curves were not linear for any of the tested bacteriophages for either sunlight-exposed or control populations (16). Consequently, for each bacteriophage survival experiment, the least-squares estimate of the linear dieoff curve was calculated by using log-transformed concentrations (23). For the experiment with phage MS2 shown in Figure 1, the exponential inactivation rate (K_e ± half of the 95% confidence interval) with sunlight exposure was 0.32 ± 0.10 h^{-1} ($N = 18$) compared with 0.006 ± 0.002 h^{-1} for an extended experiment ($N = 24$) in the dark. Bacteriophage inactivation rates from paired survival experiments (sunlight exposure and dark control) are summarized in Table I.

The effect of solar radiation on the survival of E. coli in filtered seawater is shown in Figure 2 for a typical trial. Viable plate counts (CFU mL^{-1}) with lactose nutrient agar are plotted on the logarithmic ordinate vs. duration of exposure in seawater. Survival of E. coli at 10 °C is clearly greater in the dark than with sunlight exposure. Analysis of variance, using log-transformed plate counts, revealed significant mortality for the sunlight-exposed population ($N = 15$), but not for the population kept in the dark ($N = 6$).

Eight survival experiments with E. coli populations in sunlit seawater were completed and all showed rapid mortality for sunlight-exposed cells (T90 <5 h) (16). Examination of semilogarithmic dieoff curves from these experiments indicated that E. coli mortality in sunlit seawater was not well described as an exponential decay process; that is, the curves were not linear. Rather, each curve exhibited a period (τ) of negligible mortality, ranging
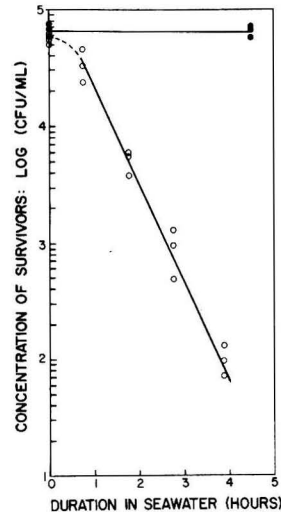
Figure 2. Effect of solar radiation on the survival of E. coli in filtered coastal seawater at 10 °C. Each data point is an independent concentration estimate of bacteria exposed to sunlight on 7/10/80 (O) or kept in the dark (●).

Table II. Mortality Parameters for E. coli Suspended in Filtered Coastal Seawater

| | | | K_e,[a] h^{-1} | |
temp, °C	date	τ, h	sunlight-exposed populations	dark/control
10	7/10/80	0.45	1.95 ± 0.24	0.011 ± 0.002
15	8/16/79	1.03	2.16 ± 0.35	0.009 ± 0.010
15	9/9/79	0.49	1.24 ± 0.55	0.005 ± 0.003
23	8/7/79	1.04	2.92 ± 0.35	0.022 ± 0.030

[a] Reported is the exponential mortality rate (K_e) and half of its 95% confidence interval. The mortality rate is the slope of the linear portion of the semilogarithmic dieoff curve, as estimated by using the least-squares criterion. For sunlight-exposed populations a brief lag period (τ) passed before exponential dieoff was observed; for populations kept in the dark, τ was zero. For E. coli, the decimal reduction time (T90) is related to K_e as follows follows:

$$T90 = (\ln 10)/K_e + \tau$$

The salinity of the seawater was 26 g kg^{-1} for the experiments at 15 and 23 °C and was 21 g kg^{-1} for the experiment at 10 °C.

from 0.4 to 1.5 h, before dieoff was observed (16). These values compare favorably with the observations of Foxworthy and Kneeling (27), who noted mortality lag times up to 2.7 h for coliform populations in sewage plumes in coastal surface waters. In contrast, there was no reason to reject the exponential decay model for E. coli populations exposed to seawater in the dark for either short (<6 h) or extended (≤437 h) duration (16).

Mortality parameters (K_e, τ) are presented in Table II for paired light–dark experiments with E. coli. For sunlight-exposed E. coli, the reported dieoff rate (K_e) is the slope of the linear, semilogarithmic dieoff curve, which was estimated by the least-squares method and was fitted to that portion of the data that exhibited mortality. For these experiments only the initial concentration estimates ($t = 0$) were not included for the log–linear curve fitting. Extrapolation of the linear portion of the semilogarithmic

Table III. Effect of Solar Longwave Radiation (λ >370 nm) on the Survival of *E. coli* and Bacteriophage MS2 in Filtered Seawater at 10 °C

duration of exposure, h	concn of survivors,[a] mL^{-1}	
	E. coli	Phage MS2
0.0	78 333 ± 2517	26 817 ± 3336
3.5	53 667 ± 5923	13 567 ± 846
6.0	30 833 ± 5686	8 600 ± 700

[a] Reported is the mean ± standard deviation of the plate counts ($n = 3$). Analysis of variance, using log-transformed concentrations, indicated significant ($p < 0.001$) lethality for both *E. coli* and bacteriophage MS2. The salinity of the coastal seawater in this experiment was 21 g kg^{-1}. The mortality rates of *E. coli* and bacteriophage MS2 were indistinguishable when exposed to filtered sunlight in this experiment, conducted on 7/14/80.

Table IV. Comparison of Exponential Dieoff Rates of *E. coli* and Bacteriophages under Identical Conditions in Sunlit Filtered Seawater

	K_e,[a] h^{-1}		
organism	expt 1 (8/22/79)[b]	expt 2 (8/16/79)[c]	expt 3 (8/15/79)[c]
phage MS2	0.50 ± 0.23	0.41 ± 0.09	0.47 ± 0.12
phage ϕx-174	0.90 ± 0.52	ND[d]	0.65 ± 0.42
phage T7	0.98 ± 0.35	ND	0.64 ± 0.19
E. coli	1.74 ± 0.60	2.16 ± 0.35	ND

[a] Reported is the exponential dieoff rate (K_e) and half of its 95% confidence interval for each survival trial using filtered coastal seawater with salinity of 26 g kg^{-1}. Single classification analysis of variance (22) of dieoff rates within an experiment shows that only bacteriophage MS2 and *E. coli* exhibit significantly different mortality rates ($\alpha = 5\%$). With the data from all three experiments, one can accept ($p < 0.005$) by using the Jonckheere–Terpstra test (28) the alternative hypothesis that the exponential dieoff rates are ranked as follows: phage MS2 < phage ϕx-174 = phage T7 ≤ *E. coli*. [b] 20 °C. [c] 15 °C. [d] Not determined.

dieoff curve toward the ordinate permitted an estimation of the lag period or shoulder duration (τ). The lag period was defined as the duration of sunlight-exposure corresponding to the initial concentration (C_0) on the linear dieoff curve (16).

During one set of survival experiments with sunlight exposure, a polyacrylic sheet, which exhibited a transmission cutoff at $\lambda \leq 370$ nm, was placed atop the inoculated beakers and water bath. Thus, it was possible to determine whether solar radiation of λ >370 nm could contribute to mortality of *E. coli* and bacteriophage MS2 in seawater. Removal of the shorter wavelengths ($\lambda \leq 370$ nm) did not eliminate the lethal action of sunlight toward *E. coli* and bacteriophage MS2 (Table III). Analysis of variance, using log-transformed concentrations, revealed statistically significant lethality in both *E. coli* and bacteriophage MS2 populations exposed to filtered sunlight but not in populations kept in seawater in the dark. Dieoff rates of bacteriophage MS2 and *E. coli* were indistinguishable under these conditions.

On three occasions, survival trials in sunlit seawater were concurrently conducted for two or more organisms. This permitted a direct comparison of in vitro mortality under identical conditions of ambient sunlight exposure. The exponential dieoff rates observed in these experiments are reported in Table IV. As shown by a single classification analysis of variance (23), the dieoff rate of bacteriophage MS2 was significantly lower than that of *E. coli* in both experiments no. 1 ($0.01 < p < 0.05$) and no. 2 ($p < 0.01$). However, the data concerning the relative susceptibility of *E. coli* and phages ϕx-174 and T7 to sunlight are ambiguous. In experiment no. 1, the exponential inactivation rates for DNA-containing phages ϕx-174 and T7 were not discernably different ($\alpha = 5\%$) from those of *E. coli* or the RNA-containing phage MS2. However, this result may be due to insufficient replication of concentration estimates during these concurrent survival trials. If the inactivation rates for the three bacteriophages were drawn from the same population, it is unlikely ($p = 0.033$) that the observed ranking of phage inactivation rates in experiments 1 and 3 would have occurred (Jonckheere–Terpstra statistic (28)). Similarly, one can accept with the data from all three experiments ($p < 0.005$) the hypothesis that the exponential dieoff rates are ranked as follows: phage MS2 ≤ phage ϕx-174 = phage T7 ≤ *E. coli* (Jonckheere–Terpstra test (28)).

Discussion

Solar Radiation as a Lethal Agent. Our data support the hypothesis that solar radiation can be an important agent controlling the distribution and abundance of *E. coli*

and viruses in coastal seawater. Experiments with pure cultures of *E. coli* and bacteriophages MS2, ϕx-174, and T7 consistently showed that in vitro microbial mortality in sunlit seawater was significantly greater than that in filtered seawater kept in the dark (Tables I and II). Consequently, our observations confirm the experimental work of Gameson and Saxon (1), who first elaborated the relationship between solar radiation and the mortality of coliform bacteria in coastal waters.

The in vitro mortality rates reported here for *E. coli* and bacteriophages in filtered seawater in the dark are comparable to those measured in the laboratory by other researchers (T90 >24 h) (7, 10–12, 15, 16). The in vitro mortality rates reported here for pure cultures of *E. coli* in sunlit seawater (T90 <4.9 h) are comparable to coliform decay rates measured during daylight hours in surface sewage plumes (T90 <5.5 h (27)). Consequently, the absence of lethal sunlight during laboratory experimentation and its presence under in situ conditions may explain why in situ mortality rates are typically higher than rates measured in vitro in the laboratory (11, 29–31). Furthermore, these favorable rate comparisons strongly support the hypothesis that solar radiation is the principal determinant of microbial mortality rate in seawater and that sunlight-induced mortality is the simplest explanation for rapid coliform mortality measured in surface sewage plumes (3). No proposed alternative mechanism of microbial mortality can account for the magnitude of and differences between reported dieoff rates for in situ and in vitro conditions (3, 16). For instance, in vitro decimal reduction times due to predation/parasitism typically exceed 24 h (7, 12), even when predator growth is stimulated by artificially large inocula of bacteria or viruses (32), and in situ concentrations of predators are even lower than those observed in vitro (3).

Despite the work of Gameson and others (1–4), solar radiation has been discounted as an agent in the ecology of enteric microorganisms in contaminated waters. This view appears to be based on the assumption that the effective wavelengths for microbial mortality do not penetrate beyond a few centimeters in seawater (33). It was shown here that solar radiation of wavelengths ≥370 nm can cause mortality in *E. coli* and bacteriophage MS2 (Table III). The depth for 10-fold reduction in spectral irradiance at 370 nm exceeds 5 m even in highly enriched

and productive seawater (34). To be sure, the principal wavelengths responsible for sunlight-induced mortality are probably those ≤370 nm (35–37). But even 305-nm radiation is reduced by only 10-fold at ca. 2 m in enriched and productive seawater (34). Finally, the objection to the "solar radiation hypothesis" on the grounds of attenuation seems to be based in part on the misconception that only far-ultraviolet radiation (λ ≤280 nm) is harmful to enteric microorganisms and that nucleic acids are the only relevant sites of photochemical damage. The results of numerous studies, including the present one, refute both assumptions (26, 35–40).

Interpretation of the Shape of Mortality Curves. In field studies of fecal coliform populations in marine surface waters, several researchers have observed convex semilogarithmic dieoff curves similar to those we observed with pure cultures of *E. coli* in filtered seawater in vitro (Figure 2); concave semilogarithmic dieoff curves have also been noted in some instances (27). The "shoulder" in the convex mortality curve has generally been attributed to transient in situ growth of cells. We propose an alternative explanation: semilogarithmic dieoff curves for *E. coli* exhibit a shoulder because mortality results from cumulative photochemical damage. Mortality curves of this shape have been frequently reported for many kinds of cells exposed to near-UV radiation, both monochromatic and broad band, and have been interpreted in this manner (35, 41). If transient growth had accounted for the mortality "lag" observed in our experiments, then we should have also observed transient growth (with specific growth rates on the order of 1.0 h^{-1}) during the first few hours of our dark survival experiments; we found no evidence for this in any of our experiments over the temperature range 10–25 °C (16, 40). Our results are consistent with those of other workers, which indicate that substrate utilization by sewage microorganisms is inhibited by inorganic salts such as sodium chloride and that excessive nutrient levels are required for coliform growth in seawater (42–44).

Comparative Survival of *E. coli* and Viruses. We observed that dieoff rates of *E. coli* in coastal seawater were significantly higher than those of bacteriophage MS2 under identical exposure to ambient sunlight (Table IV). Dieoff rates of these two organisms were not apparently different when exposed to only the near-ultraviolet (λ >370 nm) and visible wavelengths of sunlight (Table III). These results indicate the *E. coli* is more susceptible than the RNA-containing phage MS2 to the shorter wavelengths (λ <370 nm) of solar radiation. Recently, it was shown that fecal coliforms in municipal wastewater effluents are also more susceptible to 254-nm radiation, which is not present in terrestrial sunlight, than are populations of poliovirus and bacteriophage f2, both of which contain RNA (45). Data on the relative susceptibility of *E. coli* and DNA-containing phages φx-174 and T7 to ambient sunlight were ambiguous (Table IV).

For an organism, like *E. coli*, to be an ideal indicator of enteric pathogens, it is axiomatic that the indicator organism must die or multiply in the environment in an identical manner and degree (17). Differential survival of enteric bacteria and viruses have often been proposed to account for the sometimes poor correlation between concentrations of coliform bacteria and picornaviruses in coastal water samples (46–48). Our results, showing differential susceptibility of bacteriophage MS2 and *E. coli* to ambient sunlight, provide some experimental support for this explanation. Future studies should examine further the susceptibility of pathogenic and indicator microorganisms to ambient solar radiation, a potent lethal

agent in coastal marine waters.

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2,3,7,8-Tetrachlorodibenzo-p-dioxin in Sediment Samples from Love Canal Storm Sewers and Creeks

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■ Concentrations of 2,3,7,8-tetrachlorodibenzo-p-dioxin were determined in six storm sewer and creek sediment samples from the Love Canal chemical dump-site area in Niagara Falls, NY. Analysis for this highly toxic isomer by high-performance liquid chromatography (Zorbax ODS followed by partially deactivated Zorbax Sil), capillary gas chromatography (OV-17/Poly S-179), and high-resolution mass spectrometry showed concentrations from 0.9 to 312 ng/g. None was detected in an organic-rich soil sample from a rural New York State area (detection limit, 0.1 ng/g).

Introduction

2,3,7,8-Tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) is one of 22 tetrachlorodibenzodioxins (TCDDs) and 75 polychlorinated dibenzodioxins (PCDDs) that differ widely in toxicity. The highly toxic 2,3,7,8-TCDD isomer is a comparatively stable, water-insoluble molecule that is apparently not found in nature (1). PCDDs are byproducts of the commercial production of chlorophenols and related compounds (1–4). Other sources include laboratory synthesis for research purposes and production by pyrolysis at the elevated temperatures of some combustion processes, possibly municipal incinerators, industrial waste combustion, etc. (1–6).

The Love Canal is a section of an unfinished navigable hydroelectric power canal, excavated in 1894, which was to have connected the upper and lower Niagara River. From the early 1940s to 1953 municipal and chemical wastes were deposited in the canal. Our finding of measurable amounts of 2,3,7,8-TCDD in the city storm sewers adjacent to the Love Canal is consistent with the reported dumping of an estimated 200 tons of uncharacterized trichlorophenol wastes from the production of 2,4,5-trichlorophenol (7) by the Hooker Chemicals and Plastics Corp. More detailed descriptions of chemical contamination at the Love Canal are available (e.g., ref 8).

The following is part of a study by the New York State Department of Health and Department of Environmental Conservation to determine the nature and extent of contamination of the Love Canal area.

Experimental Section

Analysis of samples from a chemical dump site for 2,3,7,8-TCDD is extremely difficult. It requires (a) removal of a millionfold excess of interfering compounds through a series of chromatographic steps and (b) the ability to distinguish the 2,3,7,8-TCDD isomer in the presence of the other 21 TCDDs.

Two methods have been published that can distinguish highly toxic 2,3,7,8-TCDD in the presence of other isomers. Buser (9) used a 0.25 mm × 50 m high-resolution Silar 10C capillary gas chromatography column to separate isomers. A method published by Nestrick et al. (10) separates the 22 TCDD isomers by a combination of high-performance liquid chromatography (HPLC) and packed column gas chromatography (GC). In our laboratory the second method was modified by the use of a different solvent system, which improves the reliability of the silica gel HPLC isomer separation, and by substituting a highly selective SCOT capillary GC column coated with the Dow-developed two-component liquid phase. The capillary coating procedure is that used by Buser et al. (3). The separation of all 22 TCDD isomers under these conditions is described in a separate publication (11). Preliminary sample cleanup was made more rapid and highly selective for planar nonpolar aromatics by using an adsorptive carbon, slightly modified from that used by Stalling et al. (12). Quantitation was accomplished by ion-monitoring high-resolution mass spectrometry (HRMS) of m/e 319.8965 and m/e 321.8936 for TCDD and m/e 333.9336 for the internal standard, [U-^{13}C]2,3,7,8-TCDD, by using the Kratos MS-50 mass spectrometer at 10 000 resolution (10% valley definition).

Cleanup Procedure. Homogenized sediment (5 g) is air-dried at 60 °C, and 20 μL of [U-^{13}C]2,3,7,8-TCDD (738 pg/μL) is added. The sample is extracted by adding 25 mL of acetone and mixing thoroughly. Hexane (25 mL) is added, and the sample is stirred, extracted for a minimum of 1 h, and centrifuged. The extract is then applied directly to a 0.8 cm i.d. Amoco PX-21 adsorptive carbon (50 mg)/Celite 545 (600 mg) column and washed with 50 mL of 20% benzene/acetone. The column is reversed, and the fraction containing TCDDs is eluted with 60 mL of benzene. The volume is reduced by using a boiling water bath, and the solvent changed to 1 mL cyclohexane. The sample is then applied to a 1 × 20 cm column containing Whatman LPS-2 silica gel, which has been activated for 1 h at 130 °C. TCDDs are eluted with hexane, and the 18–36-mL fraction is collected. The sample is again boiled (benzene added) to reduce the volume to 50 μL, and the solvent is changed to toluene.

For HPLC the entire sample is injected onto two Dupont Zorbax ODS reversed-phase, 0.62 × 25 cm columns in series and eluted with methanol (2 mL/min) at 40 °C. A fraction is collected at the retention time of a 2,3,7,8-TCDD standard (14.75 min). The fraction is again boiled to 50 μL (benzene added), and the solvent is changed to iso-octane. The entire sample is injected onto two Dupont Zorbax Sil normal-phase, 0.62 × 25 cm columns in series (partially deactivated (11)), and the TCDD is eluted with a 99.3% hexane, 0.4% benzene, 0.3% water saturated dichloromethane solvent at 2 mL/min. A fraction is collected at the retention time of a 2,3,7,8-TCDD standard (13.1 min). The sample is boiled to 50 μL (benzene added), and the solvent is changed to isooctane.

GC/HRMS. Samples and standards are analyzed with a Carlo-Erba gas chromatograph/Kratos MS-50 mass spectrometer/DS-55 data system. Approximately 2 μL is injected (on-column technique) into a 0.35 mm × 35 m (HCl-etched soda glass) 60% OV-17, 40% Poly S-179 capillary GC column. Conditions are as follows: 2 mL/min He carrier; oven temperature 200 °C for 1 min, 20 °C/min to 240 °C, then hold for 30 min. The column effluent is combined with helium make-up gas and flows through a jet separator and transfer lines at 300 °C to the MS-50 source.

The mass spectrometer is tuned to 10 000 resolution at maximum sensitivity; the ion source is heated to 250 °C and operated at 70 eV with a trap current of 500 μA. Mass is calibrated with perfluorokerosene over a range of m/e 305–450. A programmable power supply controlled by the DS-55 data system changes the acceleration and electric-sector fields while keeping the magnetic field constant. This allows selection of the accurate masses of TCDDs in a high-resolution peak-scanning mode. Two ions are scanned with each injection: m/e 321.8936 and the ^{13}C-labeled internal standard at m/e 333.9336. The minimum detectable amount of TCDD under these conditions is 5 pg. If native TCDD is detected in the first injection, m/e 321.8936 and 319.8965 are monitored in a subsequent injection as verification. The data system controls the MS reference voltages so a 300 ppm scan by the analog circuitry (300 ppm mass scan range, 1000 ppm/s scan rate) is centered on the accurate mass selected. Each scan is digitized and stored while the ion current at each mass range and total ion current are displayed in real time.

Data acquired throughout the GC run are retained for processing, allowing display of single and multiple ion chromatograms, which give accurate peak retention time data. For quantitation, GC peak scans can be summed, displayed as a mass profile, and integrated. The peak area

is used to calculate the TCDD concentration with reference to the internal standard. Since mass profiles have only a 300 ppm mass range, few interferents of the same nominal mass will be detected. These will not affect quantitation as interferents such as DDE and PCB may be observed in the 300 ppm mass window but are resolved from the TCDD peak and do not contribute to its intensity.

Standards. The [^{13}C]2,3,7,8-TCDD stock standard (736 pg/μL) was obtained from the National Center for Toxicological Research. Its concentration was checked by solid-probe HRMS against a [^{37}Cl]2,3,7,8-TCDD standard, which in turn was checked against [^{37}Cl]2,3,7,8-TCDD synthesized in an earlier study (13). More recently the [^{13}C]2,3,7,8-TCDD standard has been referenced against an FDA 2,3,7,8-TCDD interlaboratory comparison standard. Our ^{13}C-labeled standard had a signal at m/e 321.8936, which was 2% of the signal at 333.9336, but at the 2 ppb spiking concentration its effect on the calculations was negligible.

The 2,3,7,8-TCDD native standard was obtained from Dow Chemical. Both its UV absorbance spectrum, obtained by HPLC/rapid-vidicon-scan UV detection (14), and its full-scan mass spectrum were obtained and verified against the literature.

The remaining 21 TCDD isomers were synthesized by pyrolysis of di-, tri-, or tetrachlorinated phenols. H. Buser (Swiss Federal Research Station) provided six pyrolysis mixtures, and D. Firestone (FDA, Washington) provided the 1,3,6,8- and 1,3,7,9-TCDD isomers. All 22 isomers have now been identified in our laboratory by using reverse-phase liquid chromatography, normal-phase liquid chromatography, capillary GC retention times, exact mass measurement, and mass peak abundance ratios.

Recovery and Precision. Recovery of [^{14}C]2,3,7,8-TCDD from sample 2 was 32% overall, as determined by liquid-scintillation counting. The preliminary cleanup, consisting of solvent extraction, PX-21 carbon, concentration–solvent change, and silica gel chromatography, had a recovery of 67% (PX-21, 90%; silica gel, 98%). The high-pressure liquid chromatography consisting of a microconcentration and solvent change, RPLC, microconcentration–solvent change, and NPLC had a recovery of 48%. This indicates a mean recovery of approximately 90% for any individual step in the cleanup procedure. The uncorrected average recovery of the [^{13}C]TCDD internal standard from the eight samples, as determined by HRMS, was 39 ± 23% (mean ± standard deviation).

Precautions. Sediment samples were collected by hand with a washed spatula and stored in the dark at 4 °C in a CH$_2$Cl$_2$-washed glass container. HPLC and syringe blanks were routinely analyzed by GC/HRMS to check for contamination. These were found to contain no TCDDs. During the analysis extracts containing TCDD were stored in Pyrex glass away from light to preclude photodecomposition.

Results and Discussion

Reliability of Procedure. The analytical method involved an exhaustive neutral cleanup, utilizing hydrophobic adsorption, hydrophilic adsorption, liquid–liquid partition and gas–liquid partition to eliminate known interfering compounds such as DDE, heptachlorobiphenyl, or trichlorophenol. Typical normal-phase HPLC and capillary GC/HRMS chromatograms and a mass profile are shown in Figures 1–3.

The effectiveness of cleanup was evidenced by the general lack of compounds other than 2,3,7,8-TCDD at the picogram-per-gram level by GC/HRMS. Because our HPLC trapping discriminated against TCDD isomers

Figure 1. Normal-phase high-performance liquid chromatogram of sample 3.

Figure 2. Single ion mass chromatograms for sample 3.

Figure 3. Mass profile for sample 3.

sample	date collected	location	description
		Table I. Samples Collected for 2,3,7,8-TCDD Analysis at Love Canal[a]	
1	11/16/79	storm sewer outflow at 102nd St. and East Niagara River	black sediment
2	3/17/80	Black Creek, south bank at 96th St. outfall	dark gray and tan clay sediment
3	3/17/80	Bergholtz Creek, south bank, 550 ft upstream of 93rd St. outfall	gray-black sediment
4	5/27/80	manhole, 97th and Frontier	dark gray and tan clay sediment
5	5/27/80	manhole, between Wheatfield and Read on 100th	black sediment
6	5/27/80	manhole, 97th and Wheatfield	dark gray and tan sediment
7	5/14/80	Hoags Corners, NY (Albany Area)	brown-black sandy soil
8		procedure with no soil	no soil

[a] Samples were selected on the basis of presence of chemical odor and oily residue.
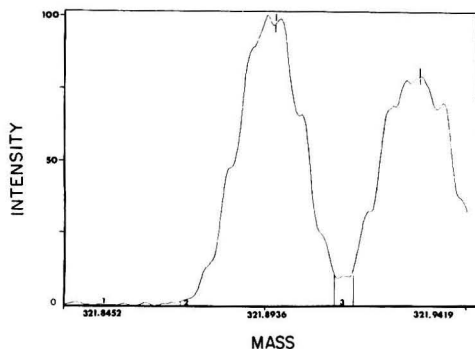
Figure 4. Mass profile for sample 1.

separated on the gas chromatograph.

The important role of HRMS in analyzing the complex mixture of chemicals in the storm sewers is shown in Figure 4. Sample 1 contained ppb levels of a non-TCDD-interfering compound having the same capillary GC retention time as 2,3,7,8-TCDD and an exact m/e of 321.9272 (TCDD = 321.8936).

A great deal of care was taken to avoid sample cross-contamination. These precautions included exhaustive glasware washing procedures. In order to be objective, we analyzed the solvent blank (sample 8) immediately after what was suspected—and later found—to be a sample containing a large amount of TCDD. This accounts for the slight presence of TCDD in the solvent blank. The syringe-soaking time was lengthened, and a control soil (sample 7) contained no detectable TCDD.

2,3,7,8-TCDD Results. The storm sewers that drained the Love Canal area prior to remedial action in 1978 are divided approximately at Read Street by a high point of elevation (Figure 5). The northern end of the canal was drained by storm sewers at 97th Street and 99th Street. These sewers flow north, connect, and empty at 96th Street into Black Creek, which drains into Bergholtz Creek and ultimately into the Niagara River and Lake Ontario. The southern end of the canal was also drained by 97th Street

other than 2,3,7,8-TCDD, other isomers may have been present in the samples but were not identified. However, 2,3,7,8-TCDD is expected to be the major PCDD produced in the alkaline hydrolysis of 1,2,4,5-tetrachlorobenzene to form 2,4,5-trichlorophenol. The most highly contaminated sample (Table I, sample 4), contained a small amount of another TCDD isomer, which was widely separated on the gas chromatograph. This isomer is one of the few that are not well resolved by HPLC from 2,3,7,8-TCDD but are well

Figure 5. Concentrations of 2,3,7,8-TCDD in Love Canal storm sewer and creek sediments, ng/g. Arrows indicate direction of flow. Manholes are shown.

Table II. Capillary Gas Chromatography (GC)–High-Resolution Mass Spectrometry (10 000) Results for 2,3,7,8-TCDD in Love Canal Storm Sewer and Creek Sediments

sample	calcd concn, ng/g dry wt[a]	GC rel retention time[b]	overall detection limit, ng/g (S/N = 2.5)	ratio, 319.8965/ 321.8936[c]
1	31	1.000	0.5	0.83
2	14	1.005	0.8	0.82
3	29	1.005	0.7	0.79
4	312	1.003	0.7	0.86
5	0.9	1.005	0.3	0.66
6	120	1.002	0.4	0.87
7	<0.1		0.1	
8	1.3		0.1	

[a] Corrected for any recovery losses by use of $[^{13}C]2,3,7,8$-TCDD internal standard; $C_1 = A_1C_2/A_2$.
[b] Relative to $[^{13}C]2,3,7,8$-TCDD internal standard at 2 ng/g. [c] Literature ratio = 0.77 (13).

Table III. TCDD Isomer Retention Index Comparison (10)

	rel retention time					
	reverse-phase HPLC[b]		silica HPLC[c]		GC (OV-17/ Poly S-179)[d]	
TCDD isomer[a]	Dow	NYS	Dow	NYS	Dow	NYS
$[^{13}C]2,3,7,8$					1.000	1.000
2,3,7,8	1.000	1.000	1.000	1.000	1.006	1.004
1,2,3,4	1.148	1.135	1.248	1.262	0.960	0.957
1,3,6,8	1.155	1.162	0.977	0.977	0.729	0.708
1,3,7,9	1.088	1.091	0.940	0.944	0.771	0.756

[a] This is a partial listing. All 22 isomers have been obtained or synthesized by the New York State Department of Health (NYS) (11). [b] NYS, 40 °C; Dow, 50 °C. [c] NYS, column deactivated, modified solvent. [d] NYS, SCOT capillary column.

and 99th Street storm sewers, which flow south, connect, and empty at the "102nd" Street outfall into the East Niagara River.

The water runoff into the storm sewers is erratic and presumably results in the transfer of both solid and liquid materials downstream. A possibility also exists for transfer of chemicals into the sewers through underground defects in the piping. In Apr 1979 a New York State survey of total halogenated organics in the storm sewer sediments identified several major entry points and showed a distribution of contaminants throughout the Love Canal sewers (8).

Sampling locations for the present study are shown in Figure 5 and described in Table I. The 2,3,7,8-TCDD results are displayed in Figure 5 and detailed in Table II. The fact that these results are specific for 2,3,7,8-TCDD was verified by comparing the retention times by three isomer-separation techniques (Table III) with those obtained by the isomer-specific method published by Nestrick et al. (10).

The storm sewer sediments contained from 0.9 to 312 ng of 2,3,7,8-TCDD/g. In contrast, the high-organic soil

control (sample 7) did not contain detectable 2,3,7,8-TCDD. These may be compared with results from a study of TCDD in 21 Love Canal storm sewer sediments by the U.S. Environmental Protection Agency that found TCDD in concentrations ranging from <detection limit to 672 ng/g (15). Our non-isomer-specific analysis of three Love Canal soils found 6.7, 0.14, and <0.0025 ng of TCDD/g (8).

The largest concentration of 2,3,7,8-TCDD in the storm sewer sediments (312 ng/g) was found immediately adjacent to the canal at its southern end (sample 4); the next largest concentration (120 ng/g) was found just upstream (sample 6). This may indicate cumulative loading from several canal points. A sample taken one street away from the canal, near the high-altitude division of the storm sewer system where little canal runoff occurs, contained only 0.9 ng/g (sample 5). The sample taken at the "102nd" Street outfall into the East Niagara River contained 31 ng/g (sample 1). The 2,3,7,8-TCDD found here may have come from either the southern end of Love Canal or the nearby "102nd" Street landfill, which also contains trichlorophenol wastes.

In the northern section of the canal a sample taken at Black Creek outfall contained 14 ng of 2,3,7,8-TCDD/g (sample 2). This may be compared with a sample taken a year earlier (Apr 4, 1979), which contained 31 ng of TCDD/g. The discrepancy may be due to environmental degradation, sample differences, or our present ability to discriminate isomers. A sample taken from adjacent Bergholtz Creek contained 29 ng/g (sample 3). A crayfish sample taken slightly upstream was previously found to contain 3.7 ng of TCDD/g.

In a recent study, fish samples taken from Bergholtz Creek, Cayuga Creek, the Niagara River and Lake Ontario were found to contain 2,3,7,8-TCDD (16).

TCDD in the Love Canal area may be associated with a heavy, chlorinated, oily residue. Since remedial action, the residue accumulates as a nonaqueous phase in the leachate holding tanks that process contaminated water from the Love Canal. A sample of this material contained 203 ng of TCDD/g (8). Significant amounts of chlorophenols have also been identified in this residue and in the leachate groundwater.

The hazard associated with human exposure to various concentrations of 2,3,7,8-TCDD is a subject of controversy, although TCDD has been found to be highly toxic, carcinogenic, and teratogenic in animal studies (see reviews in refs 1, 4, 17, 18). The extent of human exposure resulting from the presence of 2,3,7,8-TCDD in the Love Canal area is unknown.

Registry No. 2,3,7,8-TCDD, 1746-01-6.

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Effect of Simulated Acid Precipitation on Algal Fixation of Nitrogen and Carbon Dioxide in Forest Soils

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■ Three forest soils from areas exposed to acid precipitation were incubated for 21 days in the light to enhance the development of indigenous algae. The rates of nitrogen fixation (acetylene reduction) in the light and dark were significantly less if the soils were treated with simulated rain at pH 3.5 than at pH 5.6. The inhibition increased with increasing amounts of simulated rain at pH 3.5. The fixation of CO_2 in the light was significantly less in the three soils following their exposure to simulated precipitation at pH 3.5 than to the same solutions at pH 5.6, and the extent of suppression rose with increasing amounts of synthetic rain. It is suggested that algae in terrestrial ecosystems may be especially susceptible to acid precipitation.

Introduction

Algae are of considerable importance in soil. They increase the organic matter level of soil by fixing CO_2 photosynthetically. Their growth often results in improved soil structure and decreased erosion. Those blue-green algae (cyanobacteria) that fix N_2 may add nitrogen to the soil, thereby often supplying the element that frequently limits the growth of higher plants. However, because their proliferation is frequently chiefly at the surface of most soils, algae may be especially susceptible to stresses that are introduced at the surface of the soil.

One such potential stress is acid precipitation. Acidity is known to affect at least some species of algae, especially the prokaryotes. Thus, blue-green algae are reported to be rare in environments with pH values below 4.4 (1, 2), and Wilson and Alexander (3) found that nitrogen fixation and development of indigenous blue-green algae were correlated with pH of flooded soils. Similarly, Watanabe (4) reported that alkaline conditions are the most favorable for the development of blue-green algae inoculated into soil.

Because of the widespread occurrence of acid precipitation, the importance of these organisms, and their exposed position at the surface on which such rain first interacts with soil, a study was conducted to assess whether simulated acid precipitation influences algal activity. Tests were carried out on two of their most significant activities in terrestrial ecosystems, namely nitrogen fixation and CO_2 fixation.

Methods

Samples of soil were collected from the Panther, Woods, and Sagamore Lake watersheds of the Adirondacks region of New York. The pHs of the mineral layers of the surface horizons were 4.6, 4.1, and 3.9, and those of the organic layers were 4.1, 3.9, and 3.1, respectively. The soils belong to the Potsdam-Crary (coarse-loamy, mixed, frigid Typic Fragiorthod), Berkshire (coarse-loamy, mixed, frigid Typic Fragiorthod), and Adams (sandy, mixed, frigid Typic Haplorthods) series, respectively. Properties of the soils will be published elsewhere. The organic layer was col-

lected to a depth of 15 cm, and the mineral layer was from a depth of 15 to 40 cm.

Triplicate 125-g samples of mineral soil were placed in pots (10-cm diameter of top, 10 cm high), and 100 g of the organic layer was placed above the mineral soil. To enrich for algae, we incubated the soil at 23 ± 2 °C at 60% of its water-holding capacity under fluorescent lights (75 μeinstein/(s m²)) to maintain 12 h of light per day. After 21 days, the soil was treated with a total of 50, 100, 200, or 300 cm of simulated rain at pH 3.5 or 5.6 in 2, 4, 8, or 12 weeks, respectively. The simulated rain (327 mL), which was formulated as described by Evans and Raynor (5) and Cogbill and Likens (6), was applied every second day. The soils were kept in the light during the period the acid rain was being applied. The solution was adjusted to pH 3.5 with 1.0 N HCl and to pH 5.6 with 1.0 N KOH. The simulated rain was applied by pouring the solution on the soil surface, care being taken to avoid disturbing the soil.

After treating the samples with simulated rain, the pots of soil were placed in a closed system. The top portion consisted of two sheets of Plexiglas sealed together by Rez-N-Bond (Schwartz Chemical Co., Inc., Long Island City, NY). The bottom sheet had a hole of 11-cm diameter to fit the top edge of the pot, and clear silicone was placed at the edge of the hole, the silicone solidifying to hold the pot to the Plexiglas. The top sheet had a 1-cm hole fitted with serum stopper. Another sheet of Plexiglas fitted with a rubber surface was placed below the pots to provide a tight seal. Threaded rods with wing nuts were used to force the top and bottom layers close together. After 40 mL of air was withdrawn, a 40-mL portion of purified acetylene (Matheson Scientific, Inc., Bridgeport, NJ) was introduced through the serum stopper into the headspace over the soil. The final acetylene concentration was 10% by volume.

At the end of each time period, a stream of air was introduced into the pots for 2 min to remove the acetylene–ethylene mixture. The air entered through a tube inserted loosely through the hole at the top, the air exiting through the same hole. At the end of the incubation period in the light, the pots were incubated in the dark for 3, 6, and 12 h, and then air was passed through the headspace. Gas samples (5.0 mL) were withdrawn for analysis, and the remaining gas was flushed out with a stream of air.

Gas samples were analyzed by using a Perkin-Elmer (Norwalk, CT) gas chromatograph, Model 3920B, fitted with a flame ionization detector and a column (100 mm × 3.2 mm) packed with Poropak T (100 mesh). Samples were analyzed at interface 65.5 °C with H_2 at a pressure of 20 lb and air at 50-lb pressure. The flow rate of the carrier gas, N_2, was 40 mL/min. A check was run by adding water to 60% of field capacity to pots of sterile soil to obtain the recovery of ethylene. The results were corrected for the ethylene impurity in the acetylene.

After the assays of N_2 fixation were completed, the assimilation of CO_2 was measured in the same closed system and with the same soil samples. The serum stoppers were removed, and the soils were exposed to air for 2 h before conducting tests of CO_2 fixation. A 25-mL vial was then

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Table I. Effect of Four Rates of Simulated Rain at pH 3.5 and 5.6 on Acetylene Reduction in Soil

incubation	soil	pH of rain	acetylene reduction (ng of C_2H_4/(h cm^2 of soil))				
			0 cm rain	50 cm rain	100 cm rain	200 cm rain	300 cm rain
	Panther	3.5	8.31 I[a]	7.31 H	6.92 H	5.87 G	5.37 F
		5.6	8.31 C	8.90 C	9.35 D	10.9 D	12.7 E
light	Sagamore	3.5	12.8 G	8.25 F	8.15 F	7.97 F	6.82 E
		5.6	12.8 D	15.1 E	15.9 E	16.4 F	18.6 G
	Woods	3.5	8.93 G	8.59 F	8.51 F	8.08 E	7.65 E
		5.6	8.93 D	9.87 D	10.3 D	13.4 F	15.2 G
	Panther	3.5	4.97 E	3.04 D	2.83 C	2.32 B	2.10 A
		5.6	4.97 A	5.28 A	5.57 A	6.68 B	9.07 C
dark	Sagamore	3.5	3.50 D	2.18 C	1.98 B	1.93 B	1.77 A
		5.6	3.50 A	10.6 B	11.3 C	13.3 D	15.1 E
	Woods	3.5	3.90 C	4.21 D	3.86 C	3.37 B	2.95 A
		5.6	3.90 A	7.98 B	8.54 C	10.5 D	11.9 E

[a] Values for a single soil exposed in either dark or light to each pH of rain that are followed by the same letter are not significantly different at the 5% level.

Table II. Effect of Simulated Rain at Two pH Values on the Rate of Carbon Dioxide Assimilation in a 5-h Period

soil	pH of rain	CO_2 assimilated (nmol/(h cm^2 of soil))				
		before rain application	50 cm of rain	100 cm of rain	200 cm of rain	300 cm of rain
Panther	3.5	1.60 D[a]	1.33 C	1.27 C	1.15 B	1.09 A
	5.6	1.60 A	1.75 B	1.96 C	1.92 C	2.16 D
Sagamore	3.5	1.78 C	1.17 B	1.16 B	1.14 B	0.97 A
	5.6	1.78 A	2.15 B	2.27 C	2.35 C	2.66 D
Woods	3.5	1.12 D	0.95 C	0.93 C	0.84 B	0.76 A
	5.6	1.12 A	1.41 B	1.47 B	1.56 C	1.81 D

[a] Values in any one row followed by the same letter are not significantly different at the 5% level.

placed on the soil, and the system was again sealed. Radioactive CO_2 was prepared by acidifying NaH^{14}CO$_3$ (specific activity 57.2 mCi/mmol, Amersham Corp., Arlington Heights, IL). An amount of $^{14}CO_2$ equivalent to 1.0 μCi was then injected into the closed pot containing the test soil. The soils were exposed to light (75 μeinsteins/(s m^2) inside the containers). After 5 h, 4.0 mL of 2 N KOH was injected into the vial, and the remaining $^{14}CO_2$ was absorbed for 12 h by the alkali. The vial was removed, its contents were adjusted to pH 2.0 with 2 N HCl, and CO_2-free air was passed through the liquid to flush out the CO_2, which was trapped in a series of two vials containing 5.0 mL of ethanolamine (scint-analyzed grade, Fisher Scientific Co., Fair Lawn, NJ). After 20 min, 10 mL of scintillator (Aqueous Counting Scintillant, Amersham) and 30 mL of methanol (certified electronic grade, Fisher) were added to the vial. The solutions were mixed, and the radioactivity was counted with a liquid scintillation counter (Model LS 7500, Beckman Instruments, Fullerton, CA).

The values presented are the means of single determinations of three replicate pots of soil.

Results

A determination was made of the nitrogen-fixing activity of these soils after they were incubated in the light but before they received simulated rain. The rates of acetylene reduction in these forest soils are shown in Table I, and the samples are designated as receiving 0 cm of rain. All assays for acetylene-reduction activity were made at 3, 6, and 12 h, first in the light and then in the dark, but only the maximum rates in the 12-h assay period are presented. When the soils were placed in the dark, the rates of nitrogen fixation fell markedly.

The acetylene reduction was then measured in the soils that had been exposed to four rates of simulated rainfall at pH 3.5 and 5.6. The pH 3.5 simulated rain markedly inhibited nitrogen fixation in all soils as compared with

the simulated rain at pH 5.6 (Table I). The reduction in rate at pH 3.5 (as compared to pH 5.6) was significant at the 5% level at each rainfall intensity, in the light and in the dark and in all soils. The inhibitory effect increased with increasing amount of pH 3.5 rain applied. Acetylene reduction in both the light and dark was inhibited by the more acid simulated rain, and the reaction in the dark was the more sensitive to the pH 3.5 solution. In contrast with the declining rate with greater volume of simulated rain at pH 3.5, the rate increased with greater volumes of solution at pH 5.6, presumably because of the greater time periods for the responsible species to proliferate.

The rate of CO_2 fixation was significantly less (5% confidence level) in all soils exposed to simulated rain at pH 3.5 than at pH 5.6 and for each quantity of simulated rain applied (Table II). The extent of the inhibition became more marked with increasing volumes of synthetic rain applied to the soil. The increase in CO_2-fixing activity with time in the soils receiving pH 5.6 rain probably resulted from the longer incubation period.

Discussion

The rate of nitrogen fixation in the soils that were treated with simulated rain at pH 3.5 was significantly less than in soils treated with the same solutions at pH 5.6. The lowered activity was evident in samples incubated in the dark or in the light, although nitrogen fixation in the dark was lower than in the light. The inhibition of acetylene reduction by simulated acid rain may be simply a reflection of the greater hydrogen ion concentration because blue-green algae in solution are sensitive to low pH (2), but it could be a result of the greater amounts of aluminum or undissociated organic acids at the lower pH, both being toxic to at least certain groups of microorganisms (7, 8). The greater fixation of nitrogen in the light than in the dark suggests that photosynthetic microorganisms are responsible for the activity in the light, but acetylene reduction in the dark could reflect activity of

either blue-green algae or heterotrophic bacteria (*9, 10*). Thus, Jones (*11*) found that unialgal cultures of *Nostoc* continued to reduce acetylene for several hours after being placed in darkness.

Using a ratio of 3:1 for the ratio of acetylene reduced to nitrogen reduced, it is possible to estimate that the amount of nitrogen fixed in these forest soils ranged from as low as 0.06 g/(ha h) in the dark to as high as 0.62 g/(ha h) in the light. In contrast, Loftis and Kurtz (*12*) report that up to 1.3 g of nitrogen/(ha h) may be added to the soils by blue-green algae. Although these amounts of nitrogen are small, they still may be important in a forest receiving little nitrogen from other sources. In nonforest soils, however, in which algae sometimes flourish and fix appreciable amounts of nitrogen (*13*), acid rain may have a significant impact on them, especially because the position of the algae at the soil surface places them at the site where they do not have the protection from atmospheric stresses afforded by soil constituents to the subterranean microorganisms. Growth at the soil surface is true of the eukaryotic as well as the prokaryotic algae, and hence CO_2 fixation, organic matter formation, and other beneficial actions of the algal community may be significantly influenced by the prolonged exposure to acid precipitation. Therefore, additional study is required to determine whether such possible effects do indeed take place in nature.

The simulated rain was applied at greater rates than are normal in the field in order to evaluate in short periods of time what occurs in nature during a long period of exposure. Using higher than natural levels of a potential toxicant in laboratory studies to predict long-term effects at natural concentrations is a common practice in developing toxicological models to predict epidemiological consequences. Although the validity of such an approach

has often been studied in toxicology, comparable field validations at low rainfall intensities have not yet been attempted in studies of acid rain.

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Distribution of Atmospheric Nitrogenous Pollutants at a Los Angeles Area Smog Receptor Site

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■ An intensive field study of atmospheric nitrogenous pollutants was conducted at a Los Angeles area smog receptor site, during selected 1980 air pollution episodes. Highest 4-h averaged concentrations were 47 μg m^{-3} for particulate nitrate (NO_3^-) and 36 μg m^{-3} for nitric acid ($HONO_2$). $HONO_2$ and NO_3^- exhibited opposite diurnal variations. The highest peroxyacetyl nitrate (PAN) concentration recorded was 47 ppb. Methyl nitrate was consistently observed at trace levels (<5 ppb) with diurnal variations closely following those of PAN. Interferences due to PAN and to nitric acid were found to result in chemiluminescent measurements of NO_2 significantly overestimated, by as much as 50–60% of the actual NO_2 values. In air masses sampled downwind of the central Los Angeles area, emitted species of nitrogen have undergone significant oxidation, with the products PAN, $HONO_2$, and NO_3^- accounting for up to 40% of the total nitrogen. Of the two important NO_x chemical removal pathways, $NO_x \rightarrow$ PAN and $NO_x \rightarrow HONO_2 + NO_3^-$, PAN formation constitutes a major sink for atmospheric NO_x. On a nitrogen basis, PAN accounted for ~60% of the NO_x oxidation products.

Introduction

The transport, transformations, and fate of oxides of

nitrogen in polluted atmospheres have been the object of extensive research, including laboratory investigations (*1–3*) and kinetic computer modeling studies (*4, 5*). Oxides of nitrogen (NO_x) are removed from the atmosphere by physical (e.g., deposition) as well as chemical processes, the later including homogeneous (*1–5*) and heterogeneous pathways (*6–8*). Chemical removal pathways for atmospheric NO_x lead to the formation of peroxyacetyl nitrate (PAN) and nitric acid, respectively, along with trace levels of gaseous and particulate organic nitrates and other oxygenated nitrogeneous compounds (*9*).

Even though the mechanisms of these chemical reactions are now reasonably well understood, estimating NO_x removal rates via chemical pathways in ambient polluted air remains a difficult task, due in part to the fact that only a few field studies (*10, 11*) have included measurements of NO_x and of the oxidation products PAN, nitric acid, and particulate nitrate needed for the derivation of removal rates (*12*). In this study we have conducted simultaneous measurements of these major nitrogenous pollutants at a smog receptor site, Claremont, CA, located ~45 km east of Los Angeles. The study period, Sept–Oct 1980, included the most severe photochemical episodes encountered in the Los Angeles area during 1980, with several multiday

second-stage smog alerts. The results of this study are discussed in terms of the relative importance of the NO_x → PAN vs. NO_x → nitrate (nitric acid + particulate nitrate) chemical removal pathways. Other aspects of this study discussed here include the sampling of total inorganic nitrate, using dual Teflon–nylon filter units, and the significant interferences due to PAN and nitric acid when performing chemiluminescent measurements of nitrogen dioxide in polluted air. A more detailed account of this study has been reported elsewhere (13).

Methods of Procedure

Oxides of Nitrogen. Measurements of NO, NO_2, and NO_x were performed by using a Thermo Electron Corp. Model 14 B/E chemiluminescent analyzer calibrated on site at the beginning and at the end of the study (five-point gas-phase titration, 20 ppm nitric oxide in nitrogen, traceable to a National Bureau of Standards cylinder of 50 ppm in N_2 and to a certified nitrogen dioxide permeation tube). Periodic instrument zero and span checks were conducted with ultrapure air and NO gas cylinders, respectively (Scott Marrin nitric oxide = 0.43 ± 0.02 ppm). In the NO_x mode of the instrument, other nitrogenous pollutants are converted to NO and thus introduce a positive interference in the instrument response to both NO_x and NO_2. PAN and nitric acid both produce a quantitative interference (14–16) whose importance is discussed later in this article. Other interfering species include methyl nitrate (CH_3ONO_2) and higher alkyl nitrates (14), but the ambient levels of these compounds are generally too low to create a significant interference in chemiluminescent NO_x measurements.

Peroxyacetyl nitrate (PAN) is the commonly employed name for ethane peroxoic nitric anhydride, CH_3C-(O)OONO$_2$ (17). PAN measurements were performed by using a modified Varian 1400 gas chromatograph equipped with an electron capture detector, an automated 2-cm^3 sampling valve operated on a 15-min cycle, and a 6 ft × $^1/_8$ in. Teflon column, 10% Carbowax 400 on 60/80 mesh Chromosorb P operated at 30 °C with nitrogen as carrier gas (flow = 40 mL/min). On-site calibrations of the PAN gas chromatograph were performed at the beginning and at the end of the field study by using a portable PAN synthesis and calibration unit. This unit developed in our laboratory (18) consists of a photochemical flow reactor in which PAN is prepared by chlorine-initiated photooxidation of acetaldehyde in the presence of NO_2 in air (19). This unit, which allows for on-site calibration of PAN gas chromatographs in the ppb range of PAN concentrations directly relevant to ambient levels, is described in detail elsewhere (18) and only a brief summary of the experimental protocol is given here. The reactant gases, chlorine, acetaldehyde, and NO_2, are provied by permeation tubes and irradiated in pure air in a ~115 cm long × 4.5 cm diameter U-shaped flow reactor surrounded by black lights. Synthesis of PAN under these condition is qualitatively verified by Fourier transform infrared spectroscopy. The generator output, which can be varied from ~2 to ~450 ppb of PAN by dilution, is then quantitated by two independent methods, chemiluminescence and ion chromatography following alkaline hydrolysis. The alkaline hydrolysis method entails the use of NaOH microimpingers in which PAN decomposes quantitatively to acetate ion, which is in turn measured by using a Dionex Model 10 ion chromatograph. In the chemiluminescence method, the PAN effluent is directed to a Thermo Electron Corp. Model 14 B/E chemiluminescent NO_x analyzer equipped with a nylon filter, which removes the interferent nitric acid. Unreacted NO_2, if any, is also detected by the chemiluminescent instrument. This potential problem is alleviated by performing measurements by difference, i.e., with and without quantitative removal of PAN in alkaline microimpingers. Output stability, PAN output as a function of flow reactor temperature, and efficiency of the various trapping devices (nylon filter, alkaline impinger) have been established (18). Excellent agreement between the two methods has been obtained (18) at PAN concentrations ranging from ~5 to 450 ppb.

Teflon and Nylon Filter Sampling. Teflon (Millipore Corp. FALP 4700, 1-μm pore size) and nylon filters (Ghia Corp. No. M8PL, 1-μm pore size) were mounted in series (Teflon filters upstream) by using 47 mm diameter filter holders (Millipore Corp. No. 430400) and multiple holder adapters (Millipore Corp. No. 470400). The dual filter units were operated by using an automated sequential filter sampler (SFS) designed in our laboratory (20). The SFS includes a shroud poviding an inlet cutoff of ~15 μm, a modified Bendix Unico 240 cyclone separator with a cutoff of ~2.5 μm (depending upon flow rate), and a chamber housing 13 filter ports arranged in a circular pattern. The filter ports are connected to a common pump through a system of solenoid valves that allow sequential sampling of up to 12 47 mm diameter filters with the 13th filter port being used as a field control. Two SFS were employed in this study, a standard single-port SFS as described above and one dual-port SFS allowing collection of up to six consecutive pairs of parallel samples. Both SFS were calibrated on site at the beginning and at the end of the study and were operated at a flow rate of 20 L min^{-1}. Detailed protocols for SFS operations and flow calibration are given elsewhere (13). After sampling, Teflon filters were placed in petrislides, returned to the laboratory, stored at refrigerator temperature, and analyzed within a few days. Nylon filters were immersed on site in pyrex tubes containing the buffer solution employed for ion chromatographic analysis as is described below.

Nitrate Analysis. Determination of the nitrate collected on Teflon and nylon filters was performed by using a Dionex Model 10 ion chromatograph. Quality control for these analyses included daily calibration with freshly prepared KNO_3 standard solutions, replicate analysis of standard solutions and of 10% of the samples, and daily analysis of a reference standard (filter strip, 5.50 μg of NO_3^- cm^{-2}) obtained from the U.S. Environmental Protection Agency's Environmental Measurement Systems Laboratory as part of an interlaboratory audit program.

Field Operations. All field measurements were conducted on the roof of the Jacobs Science Center, a four-story building on the Harvey Mudd College campus in Claremont, CA, about 45 km east of Los Angeles. NO_x and PAN analyzers were operated continuously. Filter samples were collected on 16 selected smoggy days, Sept 15–17, 19, 20, 22, 23, and 25–27 and Oct 1–3, and 7, 8–9, 1981. The basic sampling unit consisted of a Teflon filter followed by a nylon filter as described earlier. Most samples were collected for 4 h, but 2-, 3-, and 8-h samples were also collected on Oct 8–9, Sept 19–20, and Sept 15–16, respectively.

Operational Definitions for Nitric Acid and Particulate Nitrate. The Teflon and nylon filters employed in this study as a stacked unit have been selected for their high collection efficiencies for particulate nitrate and nitric acid, respectively. Teflon filters have been shown to retain only negligible amounts of nitric acid and other gaseous nitrogenous pollutants over a wide range of laboratory and field conditions (21, 22), thus minimizing the possibility of positive error (positive "artifact") when sampling pol-

Table I. Summary of PAN and Ozone Maxima

date	PAN, Claremont		ozone maxima, ppb			
	max, ppb	time of max, PDT	Claremont[a]	Fontana[b]	Upland[b]	time of max, PDT[d]
9/19[e]	3.5	15:30	90	80	70	15:20
9/20	9	16:00	160	150	140	16:20
9/22	13	16:45	190	180	160	16:20
9/23	19	16:00	210	210	210	15:30
9/24	30	17:00	330	320	310	16:45
9/25	23	17:50	360	310	330	17:00
9/26	31	16:35	350	320	290	16:30
10/1	31	16:00	400	370	350	16:00
10/2	44	16:05	460[c]	420[c]	440[c]	16:00
10/7	44, 45, 47[c]	18:05, 18:20, 20:50	380	360	350	16:30
10/8	46	15:50	380	380	380	15:00

[a] 30 min averaged data from Kok and co-workers, Harvey Mudd College, Claremont. [b] 1-h averaged data from the Southern California Air Quality Management District. [c] Highest values for 1980. [d] In Claremont. [e] All 1980.

luted atmospheres. Nylon filters have not been as extensively characterized as Teflon filters, but data available to date indicate excellent retention for nitric acid (*15, 16, 23–26*) and negligible retention of potentially interfering species such as NO_2 and PAN (*26, 27*). However, thermodynamics considerations (*28*) and laboratory experiments (*29, 30*) suggest that particulate ammonium nitrate deposited on Teflon and other filter materials may thermally decompose (negative "artifact"), thus releasing nitric acid that will then be collected on the backup nylon filter. In addition, particulate nitrate collected on filters may react with strong acids during sampling (*29, 31, 32*), with again the evolved nitric acid being collected on the backup nylon filter in our sampling unit. The collection efficiency of nylon filters for nitric acid and for particulate nitrate has been extensively tested in this laboratory (*33*) by using two nylon filters mounted in series and operated in parallel with the Teflon–nylon filter units employed in this study, as well as by performing parallel measurement with Teflon–nylon–nylon vs. nylon–Teflon–nylon filter units. Over the wide range of concentrations and conditions studied ($[NO_3^-] = 1-44$ μg m^{-3}, $[HONO_2] = 1-36$ μg, m^{-3}, total inorganic nitrate = 5–47 μg m^{-3}, T = 10–33 °C, humidity = 16–99%, and ozone ≤460 ppb), the collection of nylon filters was ≥97% for both gaseous nitrate (nitric acid) and total inorganic nitrate (nitric acid + particulate nitrate).

In this paper, the terms Teflon filter collected nitrate and particulate nitrate are used interchangeably, as are nylon filter collected nitrate, gaseous nitrate, and nitric acid. Taking into account the possibility of negative artifact, the amount of nitrate measured on the Teflon filters may be a lower limit for the actual particulate nitrate concentration, while the amount of nitrate measured on the backup nylon filters may represent an upper limit of the actual nitric acid concentration. Whether negative artifact is significant or not, the sum of the Teflon filter collected nitrate and the nylon filter collected nitrate represents the total atmospheric inorganic nitrate.

Results

Concentrations and diurnal profiles for oxides of nitrogen and PAN are not listed here due to space limitations and are available elsewhere (*13*). Selected NO_x and PAN profiles are described in the Discussion. The highest PAN concentration, 47 ppb, was measured on Oct 7, and other PAN maxima are listed in Table I along with the corresponding ozone maxima, up to 0.46 ppm, recorded in Claremont and in nearby Upland and Fontana. PAN maxima in the range 32–51 ppb have been previously reported in the Los Angeles area, e.g., in Pasadena (*34*),
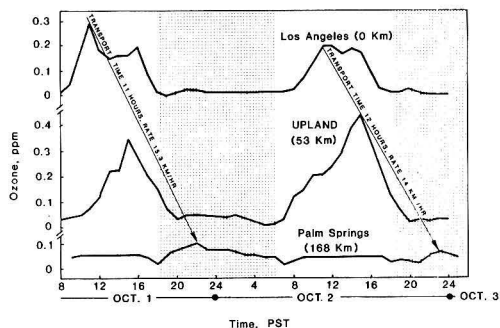
Figure 1. Ozone diurnal profiles for downtown Los Angeles, Upland, and Palm Springs, Oct 1–2, 1980.

Claremont (*35*), and Riverside (*36, 37*) during severe smog episodes.

Teflon filter and nylon filter collected nitrate concentrations are listed in Table II and have been corrected for background nitrate values derived from measurements of the nitrate content of the field control samples (1.4 and 3.2 μg for Teflon and nylon filters, respectively, which translates into ~0.3 and 0.6 μg m^{-3} for typical 4-h samples collected at a flow rate of 20 Lpm).

Discussion

Pollutant Diurnal Profiles. A good starting point in describing the diurnal variations of the measured nitrogenous pollutants is to examine ozone transport in the Los Angeles area during a typical multiday smog episode. This is illustrated for the October 1–2 episode in Figure 1, which we constructed from Southern California Air Quality Management District data. On both days ozone reached its maximum before noon in downtown Los Angeles and ~4 h later at the inland smog receptor sites including Upland and Claremont. The smog fronts reached Palm Springs (~170 km east of Los Angeles) before midnight, with averaged transport rates of 14–15 km h^{-1}.

Pollutant variations measured in Claremont were consistent with the above transport pattern. Thus, nitric oxide exhibited a morning maximum (associated, like carbon monooxide, with automobile traffic) while NO_2 exhibited a composite profile including a morning maximum (photochemical conversion of nearby-emitted NO) and a larger late afternoon maximum associated with the arrival of the smog front from Los Angeles. Diurnal PAN profiles were consistent with those expected for a secondary pollutant

Table II. Total, Teflon Filter Collected, and Nylon Filter Collected Inorganic Nitrate (μg m^{-3}), Claremont, CA, Sept–Oct 1980

date	time, PDT	total nitrate	Teflon filter (front)	nylon filter (backup)	Teflon/ nylon ratio
9/15	16–24	>4.1	ND^a	4.1	
9/16	0–8	10.2	7.1	3.1	2.3
	8–16	22.0	5.9	16.1	0.37
	18–22	14.5	2.7	11.8	0.23
9/16–17	22–02	11.7	3.7	8.0	0.46
9/17	2–6	21.1	7.5	13.6	0.55
9/19	8–11	6.3	2.1	4.2	0.50
	11–14	>1.9	1.9	ND	
	14–17	>1.7	1.7	ND	
	17–20	6.1	3.9	2.2	1.8
	20–23	5.1	3.3	1.8	1.8
9/19–20	23–2	>3.7	3.7	ND	
9/20	2–5	>3.3	3.3	ND	
	5–8	>11.9	11.9	ND	
	8–11	13.7	3.5	10.2	0.34
9/22	16–20	9.9	5.9	4.0	1.5
	20–24	7.5	6.1	1.4	4.3
9/23	0–4	30.9	29.3	1.6	18.3
	4–8	46.9	44.3	2.6	17.0
	8–12	32.5	11.5	21.0	0.55
	12–16	17.9	1.9	16.0	0.12
9/25	8–12	15.4	3.3	12.1	0.27
	12–16	20.3	2.9	17.4	0.17
	16–20	14.9	2.5	12.4	0.20
	20–24	14.0	9.8	4.2	2.3
9/26	0–4	16.1	11.9	4.2	2.8
	4–8	30.9	26.3	4.6	5.7
	9–13	32.1	5.5	26.6	0.21
	13–17	22.5	1.3	21.2	0.06
	17–21	13.7	0.7	13.0	0.05
9/26–27	21–1	7.5	2.1	5.4	0.39
9/27	1–5	18.1	13.3	4.8	2.8
	5–9	11.9	8.3	3.6	2.3
10/1	10–14	4.5	0.9	3.6	0.25
	14–18	13.3	1.3	12.0	0.11
	18–22	13.1	1.9	11.2	0.17
10/1–2	22–2	28.5	20.3	8.2	2.5
10/2	2–6	25.7	19.5	6.2	3.1
	6–10	19.5	6.1	13.4	0.45
	10–14	37.3	1.3	36.0	0.04
	14–18	23.1	0.7	22.4	0.03
	18–22	9.5	1.1	8.4	0.13
10/2–3	22–2	46.9	33.1	13.8	2.4
10/3	2–6	26.7	17.3	9.4	1.8
	6–10	30.7	14.3	16.4	0.9
10/7	10–14	39.3	5.1	34.2	0.15
	14–18	27.5	2.1	25.4	0.08
	18–22	17.3	2.5	14.8	0.17
10/7–8	22–02	42.0	28.3	14.0	2.0
	2–6	17.3	8.3	9.0	0.9
	6–10	25.9	10.1	15.8	0.6
	10–12	33.9	3.9	30.0	0.13
	12–14	21.7	1.9	19.8	0.10
	14–16	26.0	1.1	24.9	0.04
	16–18	21.8	0.5	21.3	0.02
	18–20	5.9	0.5	5.4	0.1
	20–22	6.1	3.1	3.0	1.0
	22–24	14.6	11.9	2.7	4.4
10/9	0–2	24.0	21.7	2.3	9.4
	2–4	10.6	8.8	1.8	4.9
	4–6	8.5	6.5	2.0	3.2
	6–8	12.9	11.3	1.6	7.1
	8–10	>8.7	ND	8.7	

^{a} Not determined.

Figure 2. Diurnal variations of major nitrogenous pollutants and other selected parameters, Claremont, CA, Sept 25–27, 1980.

smog formation on the following day(s) of a multiday episode (38, 39).

The gas chromatographic conditions employed for PAN measurements during this study are also suitable for the determination of several gaseous alkyl nitrates including methyl nitrate, CH_3ONO_2. A second peak with a retention time identical with that of an authentic sample of CH_3O-NO_2 was virtually always observed during smog episodes, with diurnal variations following closely those of PAN (formation mechanisms for CH_3ONO_2 in the atmosphere include the decomposition of PAN as a major pathway (38). Up to ~5 ppb of methyl nitrate were observed in Claremont during photochemical smog episodes assuming that the instrument response to CH_3ONO_2 is approximately the same as that for PAN in our conditions.

Nitrate Concentrations and Diurnal Variations. Total nitrate, Teflon filter collected nitrate, and nylon filter collected nitrate concentrations are listed in Table II. Four-hour averaged concentrations ranged from 5 to 47 μg m^{-3} for total nitrate, 1 to 44 μg m^{-3} for Teflon filter nitrate, and 1 to 36 μg m^{-3} for nylon filter nitrate. Two-, three-, and eight-hour averaged values were also within that range. The abundance of particulate nitrate in Los Angeles air, sometimes questioned by other investigators in the past on the basis of positive filter artifact considerations, is clearly demonstrated here since even our maximum measured concentration of 44 μg m^{-3} may be a lower limit if negative artifact is significant. Our maximum value for nylon filter nitrate, 36 μg m^{-3}, is equivalent to ~14 ppb nitric acid. Over the entire period studied as defined by the sampling schedule given in Table II, the average total inorganic nitrate concentration in Claremont air was ~20 μg m^{-3}. Slightly less nitrate was collected as particulate nitrate on Teflon filters (average 8 μg m^{-3} or ~42% of the total nitrate) than was collected as gaseous nitrate on nylon filters (average 11 μg m^{-3}, or 58% of the total nitrate).

of photochemical origin at a smog receptor site, with late afternoon maxima on smog episode days. Thus, PAN and ozone exhibited essentially identical diurnal variations (Figure 2) but, as noted before (36), PAN-to-ozone concentration ratios were consistently higher during nighttime. Persistence of 10–20 ppb of PAN overnight may accelerate

Table III. PAN and HONO$_2$ Interference in NO$_2$ Measurements by Chemiluminescence, Claremont, CA, Sept–Oct 1980

date	time, PDT	un-corrected NO$_2$, ppb	PAN + HONO$_2$, ppb	corrected NO$_2$, ppb	over-estimate of corrected NO$_2$, %
9/19	17–20	63	3	60	6
	20–23	74	1	73	2
9/20	8–11	66	4	62	7
9/22	16–20	68	10	58	18
	20–24	82	3	79	4
9/23	0–4	53	5	48	10
	4–8	53	4	49	8
	8–12	100	13	87	15
	12–16	89	20	69	29
9/25	8–12	119	8	111	7
	12–16	98	20	78	25
	16–20	117	23	94	24
	20–24	121	11	110	10
9/26	0–4	60	12	48	24
	4–8	65	10	55	18
	9–13	145	16	129	13
	13–17	109	27	82	33
	17–21	108	21	87	24
9/26–27	21–1	119	10	109	9
9/27	1–5	69	13	56	22
	5–9	62	10	52	19
10/1–2	10–14	41	5	36	14
	14–18	79	27	52	52
	18–22	101	22	79	28
	22–2	86	21	65	32
	2–6	48	12	36	33
	6–10	94	9	85	11
	10–14	97	35	62	56
10/7–8	10–14	134	25	109	23
	14–18	117	46	71	65
	18–22	130	48	82	58
	22–2	74	24	50	48
	2–6	35	11	24	46
	6–10	81	11	70	16
	10–14	139	24	115	21

Table IV. Distribution of Major Atmospheric Nitrogenous Pollutants, Claremont, CA, Sept–Oct 1980

date	time, PDT	concn, µg N m^{-3} NO + NO$_2$[a]	PAN	inorg nitrate[b]	ratios, % PAN/ PAN + nitrate	PAN + nitrate/ total N[c]
9/19	17–20	37	1.5	1.4	52	7
	20–23	73	0.4	1.1	27	2
9/20	8–11	45	0.2	3.1	6	7
9/22–23	16–20	35	5.0	2.2	69	17
	20–24	55	1.5	1.7	47	6
	0–4	31	2.3	7.0	25	23
	4–8	47	1.8	10.6	15	21
	8–12	60	2.9	7.3	28	14
	12–16	42	7.9	4.0	66	22
9/25–27	8–12	93	1.7	3.5	33	5
	12–16	46	7.4	4.6	62	21
	16–20	55	10.2	3.4	75	20
	20–24	81	5.4	3.2	63	10
	0–4	31	5.8	3.6	62	23
	4–8	39	4.6	7.0	40	23
	9–13	87	3.3	7.2	31	11
	13–17	49	10.8	5.1	68	25
	17–21	54	9.3	3.1	75	18
	21–1	106	4.6	1.7	73	6
	1–5	40	6.2	4.1	60	20
	5–9	32	4.8	2.7	64	19
10/1–2	10–14	21	2.2	1.0	69	13
	14–18	31	12.4	3.0	80	33
	18–22	46	10.1	3.0	77	22
	22–2	38	10.2	6.4	61	30
	2–6	21	5.9	5.8	50	36
	6–10	66	2.4	4.4	35	9
	10–14	37	12.3	8.4	59	36
10/7–8	10–14	69	7.0	8.9	44	19
	14–18	43	20.9	6.2	77	39
	18–22	50	24.2	3.9	86	36
	22–2	30	11.1	9.5	54	40
	2–6	15	4.3	3.9	52	35
	6–10	63	2.6	5.8	31	12
	10–14	65	9.7	4.2	70	18

[a] NO$_2$ corrected for PAN and HONO$_2$ interference.
[b] Inorganic nitrate = Teflon filter nitrate + nylon filter nitrate.   [c] Total nitrogen = NO + NO$_2$ + PAN + inorganic nitrate, all in µg N m^{-3}.

Gaseous and particulate nitrate exhibited nearly opposite diurnal variations, with concentration ratios ranging from 0.02 to 18.3 (Table II). As is shown in Figure 2 for a selected multiday smog episode, Sept 25–27, gaseous nitrate exhibited daytime maxima with diurnal profiles similar to those of ozone and PAN, in agreement with the photochemical origin of these three species. Particulate nitrate consistently exhibited nighttime and early morning maxima, with low daytime values of a few µg m^{-3}. As is discussed in detail elsewhere (40), these low daytime values for particulate nitrate can to a large extent be explained on the basis of thermodynamics (equilibrium) considerations for ammonium nitrate, the major component of nitrate aerosol in Los Angeles air (11).

Total inorganic nitrate concentrations exhibited composite diurnal profiles, with both daytime and nighttime maxima. During daytime, most of the nitrate is present as nitric acid. The major daytime nitric acid production pathway is that involving reaction of nitrogen dioxide with the hydroxyl radical (5). For a range of NO$_2$ and OH concentration of 0.05–0.25 and (1–3) × 10^{-7} ppm, respectively, and with use of literature kinetic data (41), nitric acid is produced at a rate of ~5–75 ppb/h. These estimated production rates are more than sufficient to account for our daytime nitric acid observations. The nighttime situation is more complex and probably involves several competing nitrate formation mechanisms. The decomposition of PAN in the presence of NO provides a source of OH radicals (38), which in turn react with NO$_2$ to produce nitric acid. On the basis of the nighttime PAN and NO$_x$ levels we measured during multiday episodes, this pathway may contribute to the still significant levels of nitric acid we observed at night (up to 15 µg m^{-3}). The heterogeneous hydrolysis of N$_2$O$_5$ (formed by the sequence O$_3$ + NO$_2$ → NO$_3$ + O$_2$, NO$_3$ + NO$_2$ = N$_2$O$_5$) probably contributes to nitric acid production in the early evening, when high levels of O$_3$ and NO$_2$, as well as lower sunlight intensity (the nitrate radical NO$_3$ photolyzes rapidly) are conductive to higher levels of NO$_3$ (42). Nitrate production via heterogeneous pathways involving incorporation of NO$_2$ and HONO$_2$ into aqueous aerosols is higher at nighttime and at lower temperatures (7, 8). These heterogeneous processes are also expected to contribute to the nighttime nitrate measured in Claremont air.

Positive Interference from PAN and HONO$_2$ in NO$_2$ Measurements. As discussed earlier, chemiluminescent NO$_x$ analyzers respond quantitatively to PAN and to nitric acid in the NO$_2$ mode of the instrument (14, 16). Since both PAN and HONO$_2$ are formed in chemical reactions consuming NO$_2$, the possibility for significant interference is greatest during severe photochemical episodes. This is evident from data in Table III, where PAN, HONO$_2$, and uncorrected and corrected NO$_2$ levels are listed for all sampling periods for which these parameters were measured simultaneously. On relatively clear days, the combined interferences from PAN and HONO$_2$ is small
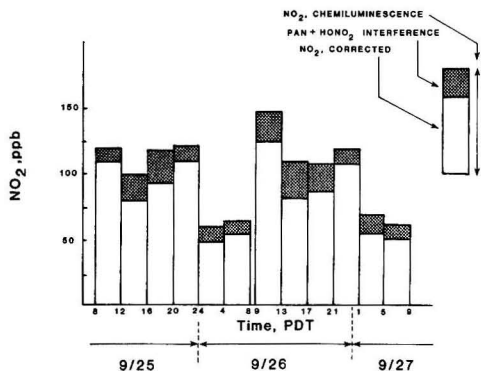
Figure 3. Ambient NO_2 levels, Claremont, CA, Sept 25-27, 1980, with and without correction for interference from PAN and $HONO_2$.

(e.g., see Sept 19 and 20 in Table IV, interference = 2-7%) and is probably not significant when compared to the combined uncertainties inherent to the measurement methods. On smoggy days, however, NO_2 can be seriously overestimated if the response of chemiluminescent instruments to PAN and $HONO_2$ is not taken into account. For example, measurements conducted around the clock during the Sept 25-27 smog episode show that NO_2 was overestimated by 19% over that 48-h period. Maximum NO_2 overestimates were 33%, 56%, and 65% (4-h averages) during the Sept 25-27, Oct 1-3, and Oct 7-9 smog episodes, respectively. As is shown in Figure 3, the interference is greatest in the mid and late afternoon when both PAN and $HONO_2$ are present at high levels (and when the contribution of particulate nitrate negative artifact, if any, to the measured nitric acid levels is minimum). This significant PAN and $HONO_2$ interference may have implications for monitoring, modeling, regulatory, and other issues pertaining to NO_2 measurements.

Relative Importance of $NO_x \rightarrow$ PAN and $NO_x \rightarrow$ Nitrate Atmospheric Reaction Pathways. From the simultaneous measurements of NO, NO_2, PAN, and nitrate conducted during this study, additional quantitative information can be gained concerning the transformations of atmospheric NO_x during photochemical episodes. Listed in Table IV are concentrations and concentration ratios of the nitrogenous pollutants of interest, i.e., NO + NO_2 (with NO_2 corrected for PAN and $HONO_2$ interference), PAN, and total inorganic nitrate, all expressed in the same mass concentration units as nitrogen (μg of N m^{-3}). Minor atmospheric products of NO_x oxidation such as methyl nitrate, other gaseous alkyl nitrates, and particulate organic nitrates are not included.

Two important observations can be derived from the data in Table IV. First, polluted air masses reaching Claremont (~4-5 h downwind from downtown Los Angeles (see Figure 1)) contain significant amounts of NO_x oxidation products, with PAN and nitrate accounting for up to 40% of the "total nitrogen" (NO + NO_2 + PAN + $HONO_2$ + NO_3^-, all expressed in μg of N m^{-3}) during smog episodes, as compared to only 2-8% on relatively "clean" days (e.g., Sept 19 and 20). The 24-h averaged products/total nitrogen ratios during multiday smog episodes were 17% on Sept 22 and 23 and Sept 25 and 27, 24% on Oct 1 and 2, and 30% on Oct 7 and 8. Second, PAN constitutes a major sink for atmospheric NO_x, accounting typically for 30-80% of the NO_x oxidation products. On a nitrogen basis, PAN was more abundant than inorganic nitrate in Claremont air on smoggy days, accounting for

~60% of the NO_x oxidation products during multiday photochemical episodes: 59% on Sept 25 and 27, 57% on Oct 7 and 8, and 62% on Oct 1 and 2, during which the highest ozone levels for 1980 were recorded.

Comparison with Other Studies. As mentioned earlier in this article, only a limited number of field studies conducted in the Los Angeles area have included simultaneous measurements of the nitrogenous pollutants of interest. Grosjean and Friedlander (11) reported PAN/NO_3^- ratios of 1.4-4 (μg of N m^{-3} basis) in Pasadena, CA, during the July 25, 1973, smog episode. Nitric acid was not included. Spicer (10) conducted measurements of PAN, $HONO_2$, NO_x, and particulate nitrate in West Covina, CA, in Aug-Sept 1973. One-hour averaged maxima were 90-270 ppb for ozone, 3-46 ppb for PAN, and 0-40 ppb for nitric acid. One-hour averaged PAN + $HONO_2$/NO + NO_2 + PAN + $HONO_2$ ratios ranged up to 54% (ppb basis). Particulate nitrate data were not included in these calculations since only 24-h averaged values were obtained. Tuazon et al. (35) reported PAN/$HONO_2$ ratios of 0.3-0.8 (ppb basis) in Claremont, CA, during 1978 smog episodes. Particulate nitrate was not measured. More recently, Hanst et al. (43) reported 3-12 ppb nitric acid and 3-16 ppb PAN in Los Angeles, on June 26-27, 1980, with PAN/$HONO_2$ ratios of 0.6-2.2 (ppb basis). Particulate nitrate was not measured. Thus, the results of this study are consistent with those of previous investigations with respect to PAN and $HONO_2$ concentrations, PAN/$HONO_2$ ratios, and products/gas-phase nitrogen ratios. Time-resolved products/total nitrogen ratios have not been presented prior to this work.

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Aerosol Filtration by a Cocurrent Moving Granular Bed: Penetration Theory

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■ A penetration model for aerosol filtration by a cocurrent moving bed of granules has been developed. The model incorporates straight-through penetration and reentrainment of previously collected dust, the latter due to granule motion, both mechanisms having been found significant in experiments. The model, an extension of classical clean granular bed theory, utilizes the familiar concept of a single-granule coefficient for collection and proposes a similar coefficient for reentrainment. Reentrainment was found in experiments to be a function of particle size and other factors such as gas velocity, granule velocity, and the extent of intergranular dust deposit. The single-granule reentrainment coefficient for moving granules, n_R, was found to depend upon the product of intergranular dust deposit and the square root of dust-particle diameter $(Kd_p^{1/2})$ for particle diameters between 0.16 and 5.5 μm.

Introduction

Granular bed filters are of interest for collection of particles from hot gas streams in advanced power-generation systems such as combined cycle coal gasification or pressurized fluidized bed coal combustion (1–7). A recent review of granular bed filtration theory and experiments is provided by Yung et al. (8). A common feature of practical granular-bed filters is bed motion for granule cleaning and recharge and for control of pressure drop.

Most previous experiments and theory concerned stationary clean beds. Theoretical prediction of particle collection by granules commonly involves solving equations of motion for particle trajectories accounting for collection forces and the flow field around an isolated collector. Common assumptions include (1) low dust concentration in the gas, (2) no dust accumulation on the collectors, and (3) complete retention of all particles that contact a collector (9). These studies are useful to explain results from clean-bed experiments but have not been extended to more practical, loaded-bed cases.

Recent theoretical studies to model loaded granular beds by Payatakes et al. (10, 11) and Goren (12) consider enhanced particle collection by previously captured particles as well as reentrainment of collected particles. These authors show that hydrodynamic factors affecting particle collection by already deposited particles or by dendrites near the surface of a granule are complex. Factors affecting reentrainment are also poorly understood. However, reentrainment in moving granular bed filtration experiments significantly affects overall bed efficiency (7, 13). A penetration model for a moving granular bed filter must account for reentrainment related to granular motion.

This paper presents a theoretical treatment of particle penetration through a cocurrent moving granular bed filter (CMGBF). The present model explicitly accounts for reentrainment as a particle penetration mechanism, in addition to penetration due to failure to collect, i.e., penetration straight through. Data are provided that characterize the factors affecting reentrainment.

Penetration Model

A previous study (13) of CMGBF performance showed that some dust penetrates straight through and some

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captured dust is reentrained due to granule motion. Furthermore, penetrating dust from these two sources had different size distributions. This paper considers these two separate penetration mechanisms and discusses a model that is an extension of the classical clean granular bed filtration model, to which it reduces when reentrainment is negligible.

Mass Balance on the Aerosol. In the CMGBF shown in Figure 1, clean granules and dusty gas are added continuously at the bed top, then pass downward cocurrently, and exit at the bed bottom. A unique feature of the CMGBF is the controlled formation of an intergranular dust deposit to ehance filtration of submicron particles. A mass balance on the aerosol in the differential volume, $A \, dZ$, is

$$\text{rate in} = \text{rate out} + \text{accumulation}$$

$$Q_g C = Q_g (C + dC) + E - R \quad (1)$$

where E = collection rate and R = reentrainment rate. Solution of eq 1 requires expressions for the differential collection and reentrainment rates.

Particle Collection Rate. Consider particle collection analogous to classical clean-bed theory except that the single-granule collection coefficient, η_G, accounts for the effect of dust adhering to the granule as well as for the granule itself.

The collection rate, E, can be expressed as the product of the cross-sectional area swept clean by these collectors and the particle flux through the differential volume:

$$E = A \, dZ (1 - \epsilon_o) \frac{\pi d_G^2/4}{\pi d_G^3/6} \eta_G C \frac{V_g}{\epsilon} \quad (2)$$

In eq 2, the fraction of the differential volume occupied by granules is indicated by 1 minus the clean bed porosity, ϵ_o. The porosity, ϵ, in the flux expression is the effective porosity accounting for reduced voidage due to the intergranular dust deposit. The superficial gas velocity, V_g, divided by the effective porosity, ϵ, is the interstitial gas velocity. Equation 2 is developed by assuming particle collection in the dirty bed remains related to the granules, that is, complete "cake filtration" does not occur here as it would if all void space were entirely dust filled.

Particle Reentrainment Rate. Consider a particle reentrainment rate, R, based on removal of dust already collected and adhering to the granule surface. The expression for the mass of collected dust in the differential volume is

$$m = s_p \rho_p A \, dZ \quad (3)$$

where ρ_p = dust particle density (kg/m³) and s_p = solidity of dust deposit (volume of dust/volume of bed, dimensionless).

Next define a gas parcel as the gas volume equivalent to the volume of a single granule. The number of gas parcels per second passing each granule is given by

$$N = \frac{\pi d_G^2/4}{\pi d_G^3/6} \frac{V_g}{\epsilon} \quad (4)$$

A dimensionless single-granule reentrainment coefficient, η_R, will now be defined as the fraction of all dust adhering to a single granule that is reentrained from that granule

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Note: Z positive in downward direction
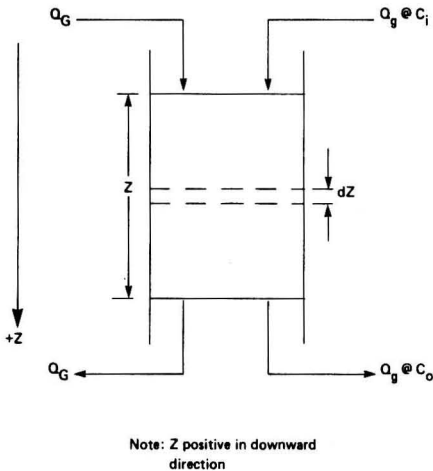
Figure 1. Schematic diagram of CMGBF.

by a single gas parcel passing it. The reentrainment rate in the differential volume is the product of eq 3, 4, and the single-granule reentrainment coefficient:

$$R = \frac{3}{2} \frac{V_g}{\epsilon d_G} \eta_R s_p \rho_p A \ dZ \qquad (5)$$

Substituting eq 2 and 5 into eq 1 gives an expression for the mass balance on the aerosol:

$$dC = -\frac{3}{2} \frac{dZ}{\epsilon d_G} [(1 - \epsilon_o) \eta_G C - s_p \rho_p \eta_R] \qquad (6)$$

Before eq 6 can be integrated across the depth, Z, of the bed, an expression for s_p in terms of dust concentration, C, is required.

Mass Balance at Steady State. The CMGBF is designed for continuous operation, and at steady state all dust that enters the bed must leave in the aerosol stream or on the granules. With the assumption that dust entering on the granules is negligible, a mass balance at steady state on total dust in the aerosol and on the granules yields

$$Q_g C_i = Q_g C + Q_G s_p \rho_p / (1 - \epsilon_o) \qquad (7)$$

Solving eq 7 for s_p produces

$$s_p = Q_g (C_i - C)(1 - \epsilon_o)/(Q_G \rho_p) \qquad (8)$$

where C_i = entering aerosol concentration (kg/m³). Substituting eq 8 into eq 6 yields

$$dC = -\frac{3(1 - \epsilon_o)}{2 \epsilon d_G} \left[C \left(\eta_G + \eta_R \frac{Q_g}{Q_G} \right) - \eta_R C_i \frac{Q_g}{Q_G} \right] dZ \qquad (9)$$

Integration of eq 9 yields

$$Pt = \frac{C_o}{C_i} = \left\{ \eta_R \frac{Q_g}{Q_G} + \eta_G \exp \left[-\frac{3}{2} \frac{1 - \epsilon_o}{\epsilon} \frac{Z}{d_G} \left(\eta_G + \eta_R \frac{Q_g}{Q_G} \right) \right] \right\} \Big/ \left\{ \eta_G + \eta_R \frac{Q_g}{Q_G} \right\} \qquad (10)$$

This is the theoretical expression for steady-state particle collection and reentrainment in a cocurrent moving granular bed filter operating under the conditions of a continuous dust feed rate at constant concentration. These assumptions are appropriate for the CMGBF operating in

a continuous mode with a steady-state dust deposit. It cannot be used if the inlet concentration varies significantly or is zero. Equation 10 does not describe transient responses such as initial deposit buildup or deposit deterioration when the dust feed stops.

Equation 10, which is general, can be applied to particle collection in any cocurrent moving granular bed, whether collected particles reentrain or not. If no reentrainment occurs ($\eta_R \rightarrow 0$), eq 10 reduces to the classical granular bed penetration equation (4, 14, 15):

$$Pt_{\eta_R \rightarrow 0} = \exp \left[-\frac{3}{2} \frac{1 - \epsilon_o}{\epsilon} \frac{Z}{d_G} \eta_G \right] \qquad (11)$$

For a demonstration of the effect of reentrainment on bed performance, consider the situation when the bed is very deep, i.e., $z \rightarrow \infty$; in this case

$$Pt_{z \rightarrow \infty} = \frac{\eta_R}{\eta_G} \frac{Q_g}{Q_G} \Big/ \left[1 + \frac{\eta_R}{\eta_G} \frac{Q_g}{Q_G} \right] \qquad (12)$$

Even if particles are collected efficiently, i.e., $\eta_G \rightarrow 1$, significant penetration may occur if reentrainment is important, $\eta_R > 0$.

Discussion of Theory

Effective Porosity. In the integration of eq 9, it was assumed that the effective porosity, ϵ, is independent of bed depth. This approximation is valid when the steady-state dust deposit is established near the bed surface so that it does not vary appreciably throughout the bed depth. For the experimental operating conditions described below, pressure-drop data at intermediate bed depths indicated that a stable deposit was formed within 2 or 3 cm of the bed surface in 13-cm deep beds.

One of the unique features of the CMGBF is its ability to function as a "graded media" filter, i.e., larger dust particles are collected on clean granules at the bed surface while smaller particles are collected within the bed pores by an increasingly dense dust deposit. An optimal CMGBF design may be one in which graded media filtration is achieved throughout the bed depth. However, some depth of a uniform dust deposit appears desirable to collect submicron particles that might otherwise penetrate, but an excessively deep bed may result only in pressure drop and reentrainment penalties. As demonstrated previously (13), the CMGBF can provide high collection efficiency with a shallow bed; however, particle reentrainment must be controlled to maintain low overall penetration.

For the steady-state dust deposits achieved in our experiments, the solidity of the dust, s_p, was less than 0.04, i.e., more than 90% of the clean-bed void space remained open. However, the effective porosity, ϵ, may be estimated by

$$\epsilon = \epsilon_o - s_p \rho_p / \rho_{bp} \qquad (13)$$

where s_p = solidity of dust deposit (dimensionless), ρ_p = dust particle density (kg/m³), and ρ_{bp} = loose bulk density of dust (kg/m³). Equation 13 reflects the fact that, due to higher resistance to airflow through the dust deposit, essentially all gas flow occurs through the dust-free void space between granules. Equation 13 can be used to estimate the effective porosity, ϵ, utilized in eq 10.

Factors Affecting Reentrainment. Although many theories are available to describe clean-granule efficiency, no adequate theories are presently available to predict the single-dirty-granule efficiency, η_G, or to predict the single-granule reentrainment coefficient, η_R. As a first ap-

proximation, a lower bound for efficiency of the conditioned granule, η_G, might be calculated from theory for clean, unconditioned granules. Reentrainment should depend upon the ratio of separation force to adhesion force for particle-to-granule and particle-to-particle interactions. A review of the literature suggests that these forces, for other than the most simple configurations, are poorly understood and cannot be predicted accurately.

Adhesion forces include van der Waals, electrostatic, and surface tension capillary forces. As humidity increases, capillary forces become more singificant and electrostatic charges leak away. In general, adhesive forces increase with particle size (16). Corn (17) gave expressions for van der Waals forces and capillary forces acting between a spherical particle and a surface that show that these forces are directly proportional to particle diameter.

Separation forces should be related to air drag and mechanical shear, the latter caused by granule slippage. For small particles in the Stokes region suspended in air, drag force is proportional to particle diameter. Thus, the ratio of separation force to adhesion force, were only simple Stokes drag to apply, would be independent of particle size. However, because particles are attached to granules or other particles, the flow fields around attached particles are complex, as a velocity gradient exists near a granule's surface. Fuchs (18) indicated that two attached particles in a velocity gradient experience a separation force related to the second power of particle diameter. Goren and O'Neill (19) determined the drag force on a particle attached to a granule ($d_p \ll d_G$) from solution of Stokes equations accounting for the velocity gradient near the granule's surface. If a linear shear flow is assumed, drag force is again found proportional to the square of particle diameter. Consideration of the latter two relationships for separation force suggests that reentrainment, as defined by the ratio of air-drag separation force to adhesion force, should be proportional to the first power of particle diameter. Theoretical considerations, therefore, suggest that reentrainment related to air drag may depend on particle diameter raised to some power between 0 and 1.

However, experiments with a CMGBF, as reported previously (13), indicated simple air drag in a stationary bed loaded with dust did not produce significant reentrainment. At the controlled steady-state dust loadings in these experiments, the CMGBF was not at the "saturation point" as described by Taub (20). Significant reentrainment from the CMGBF occurred only when the bed was moving. Thus, reentrainment from the CMGBF, on a microscale, appears to involve shear forces associated with granule motion that overcome particle adhesion forces and facilitate resuspension of separated particles by air drag.

Analyses of the distribution of forces in moving granular beds as developed for applications such as fluid catalytic crackers, pebble heaters, and crystal washers appear applicable to the CMGBF as well. Delaplaine (21) studied forces acting in granular solids flowing downward under the influence of gravity, and Brandt and Johnson (22) extended this one-dimensional flow model to include stresses included by interstitial flow. A two-dimensional model accounting for interstitial flow axially and transversely toward exit screens was developed by Grossman (23). These theoretical developments involve solution of elemental force balances for three normal (compressive) stresses and six shear stressed by using appropriate assumptions.

General conclusions from these studies are that pressure drop from fluid flow can be incorporated as an additional body force similar to gravity. Stress is distributed by granule-to-granule friction, and no equilibrium shear stress can exist greater than that determined by internal bed friction. If the ratio of shear to normal stresses at a location becomes equal to or greater than the coefficient of internal friction, slippage will occur, and a new stress distribution will develop. For the cocurrent mode, equilibrium stresses, including shear, increase with bed depth, pressure drop, granular bulk density, and column diameter to an asymptotic value which is independent of depth in deep beds, $Z/D > 5$ according to Delaplaine (21).

Delaplaine (21) found, in experiments with glass beads or sand flowing in tubes with tube-to-granule diameter ratios greater than 20, that approximately 80% of the bed cross-sectional area in the central core flowed in a cohesive, rodlike manner, and shear occurred in the outer 20% of the flowing bed. Toyama (24) observed similar flow regions in a glass-front rectangular bed by using layers of different colored granules and reported that the shear region at the wall was 4–8 granule diameters thick. Grossman (23) showed calculated shear stress profiles at various bed depths and radical positions that indicate maximum shear stress at the wall and rapidly decreasing shear stress away from the wall, particularly for shallow beds ($Z/D < 2$). According to Grossman (23), shear stress at the wall increases with the wall friction coefficient, μ', and decreases with the internal friction coefficient, μ. The coefficient of friction at the wall, μ', was not found to be a function of bed velocity or granule size in Delaplaine's experiments with dry systems and no interstitial fluid flow. Brandt and Johnson (22) found a slight increase, about 25%, in μ' over a bed velocity range of 0–5 mm/s (30 cm/min) for 20–40 mesh ion-exchange resin in a lucite tube with cocurrent water flow, and the μ' was independent of the relative fluid velocity through the bed.

These studies suggest that within the CMGBF there exist axial and radial distributions of compressive and shear forces acting on the granules and adhering dust. It is likely that the presence of dust on the granules alters the friction coefficients μ and μ' compared to clean granule friction coefficients. Within the plug-flow portion of the bed, the dust layer on a granule may be stable and perhaps compacted. However, near the wall, shear stresses become large and cause granule slippage. If, at the onset of slippage, the shear forces overcome particle adhesion forces, particles will separate and may be resuspended by interstitial gas flow. On this basis, the reentrainment coefficient, η_R, should increase in conjunction with factors that increase shear stress within the bed such as bed depth ($Z/D < 5$), granular bulk density, column diameter, and pressure drop from cocurrent fluid flow. The maximum shear stresses that can develop will depend on the friction coefficients, μ and μ', which in turn are influenced by the presence of the dust and must be determined empirically.

Temperature Effects. The single-granule collection coefficient, η_G, and the single-granule reentrainment coefficient, η_R, contain the functional relationships with respect to particle size, gas velocity, and other factors including temperture. The predicted trends of particle collection at temperatures different from ambient can be estimated by inspection of the temperature-dependent terms in the single-granule collection coefficients for impaction, diffusion, and sedimentation. In general, high temperature is expected to reduce the collection efficiency for particles larger than a few tenths of a micron in diameter. Adhesion and drag forces that affect particle reentrainment also change at elevated temperatures. For example, capillary force will decrease at high temperatures,

Table I. Experimental Conditions

	block I				block II				block III		
run no.	K^a	$V_G{}^b$	$V_g{}^c$	run no.	K^a	$V_G{}^b$	$V_g{}^c$	run no.	K^a	$V_G{}^b$	$V_g{}^c$
18	1.3	0.026	261	13	1.3	0.026	139	4	0.5	0.037	200
17	3.7	0.026	139	12	3.7	0.026	261	6	4.5	0.037	200
16	1.3	0.049	139	9	1.3	0.049	261	3	2.5	0.019	200
20	3.7	0.049	261	11	3.7	0.049	139	7	2.5	0.056	200
15	2.5	0.037	200	14	2.5	0.037	200	2	2.5	0.037	100
19	2.5	0.037	200	10	2.5	0.037	200	1	2.5	0.037	300
								5	2.5	0.037	200
								8	2.5	0.037	200

^{a} K = intergranular dust deposit ratio (% by weight). ^{b} V_G = granule velocity (mm/s). ^{c} V_g = superficial gas velocity (mm/s) (bed depth = 130 mm and granule diameter = 2.1 mm for all runs).

and air drag will increase for particles large than a few tenths of a micron in diameter. However, ash particles may become sticky and thereby reduce reentrainment. The proposed single-granule coefficients should be useful to correlate results of empirical studies to characterize selected dust-granule systems at elevated temperatures.

Experimental Section

Experiments were performed to quantify the coefficients η_G and η_R in eq 10 and to investigate the functional relationship of factors affecting reentrainment.

The CMGBF consisted of three gas-tight sections: a granule storage bin, a 203-mm diameter bed column, and a granule control mechanism. Granules flowed by gravity downward through the column, concurrently with the gas flow. Cleaned gas exited through a circumferential gas-exit screen located below the active filtering porition of the CMGBF. High density (ρ_G = 3250 kg/m^3) alumina granules with a diameter of average mass of 2.1 mm were used for all runs. All runs were at ambient temperature and pressure. The experimental apparatus is described in detail elsewhere (25).

The test aerosol was electrostatically precipitated fly ash from a utility boiler fired with pulverized coal. The fly ash was resuspended by an NBS dust feeder (26) and had a count median diameter of 0.3 μm. Samples for particle size analysis were isokinetically collected on Nuclepore filters. Photomicrographs were obtained by scanning electron microscope (SEM), and particles were sized and counted with a Zeiss MOP image analyzer.

Twenty runs with the CMGBF were conducted in a "central composite design" experiment (27) with three control variables: V_g, superficial gas velocity; V_G, granule velocity; K, the ratio of collected dust mass to granule mass within the conditioned bed at steady state. The nominal factor levels are shown in Table I. All experiments described here were conducted at constant bed depth and granule size; effects of these factors were reported in a previous paper (13).

The weight ratio, K, is an experimental surrogate for the dust solidity within the bed, s_p. The relationship between these variables is

$$s_p = (1 - \epsilon_o)\rho_G K/\rho_p \qquad (14)$$

where s_p = dust solidity (dimensionless), ϵ_o = porosity of clean bed (dimensionless), ρ_G = granule density (kg/m^3), ρ_p = dust particle density (kg/m^3), and K = ratio of dust mass collected to granule mass in the bed (kg/kg). Although dust solidity within the bed, s_p, could not be measured directly, ratio K could be measured and used to calculate s_p through eq 14.

A series of end-of-run penetration measurements were conducted to identify the significance of penetration

mechanisms including (A) straight-through penetration, (B) air scouring, and (C) reentrainment caused by granular motion. After the normal penetration measurements were completed, bed motion was stopped and penetration was immediately measured again. This dust-on/bed-stopped situation measured the penetration straight through the loaded bed. Next the dust feeder was stopped and the downstream concentration was determined with the bed still motionless to measure the effect of the air scouring at the superficial gas velocity of the run. Finally the bed motion was restarted but with no dust fed. This dust-off/bed-moving situation allowed sampling of the dust initially collected but subsequently reentrained from the loaded bed as the result of granular motion.

Mass penetration and pressure drop data for all runs shown in Table I are reported elsewhere (25).

Penetration data by count in particle size categories between 0.08 and 7.3 μm were obtained for runs 1-9. Fractional penetration data were obtained for these nine runs for the conditions of (1) an initial clean moving bed when dust feed began, (2) a normal cocurrent steady-state bed at the end of at least two bed volume replacements, and (3) straight-through penetration of the stationary loaded bed. Particle size distributions were also obtained for these nine runs for the particles reentrained from the moving bed when dust feed had stopped. Particle size information obtained from runs in block III allows comparison of the effect of each control variable at its extreme and center-point conditions. Center-point conditions are replicated for error determination.

Average fractional penetration data for runs 1-9 are shown in Figure 2 for the moving and stationary loaded bed cases. Penetration in the submicron range was approximately the same whether the loaded bed was moving or not; however, penetration in the larger particle sizes was clearly greater when the loaded bed was moving. The relatively greater variability in the penetration data for the normal moving bed is due to the influence of control variables, other than particle size, not separated in this crude average but discussed below. Straight through penetration was influenced much less by these factors, as indicated by reduced variability in the lower curve in Figure 2.

Particle size data from the photomicrographs clearly showed that the reentrained particles were larger than the particles penetrating straight through the stationry loaded bed. Very small particles (approximately less than 0.3 μm) were not found on the photomicrographs of reentrained particles, suggesting that small particles were not reentrained.

Although agglomerates were present in the reentrained particles as observed on SEM photomicrographs, the proportion of agglomerates in any size category was not significantly different from the proportion of agglomerates
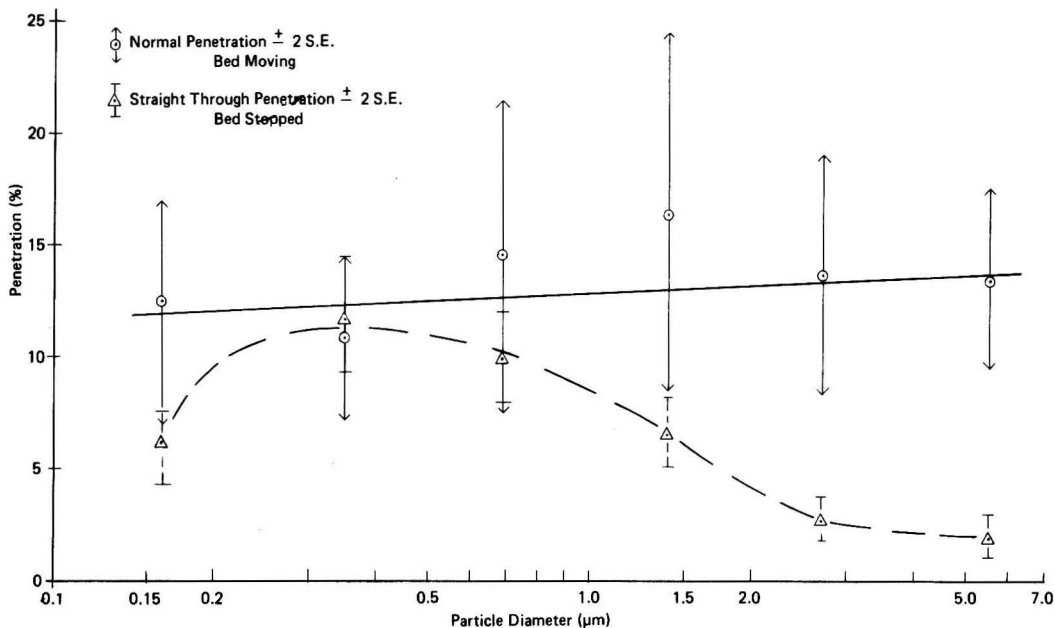
Figure 2. Average penetration vs. particle size for runs 1–9.

in the same size category either upstream of the CMGBF or in the particles penetrating straight through. The fly ash was well combusted and consisted of glassy spheres, which normally do not agglomerate appreciably. Thus, it appears that most particles penetrated or were reentrained without significant additional agglomeration.

Evaluation of Single Granule Reentrainment Coefficient

Reentrainment due to granular motion is exemplified by the difference between penetration when the bed is operating normally and straight-through penetration immediately after the bed is stopped. The increased penetration due to reentrainment in larger particle sizes can be seen in Figure 2. These fractional penetration data were used to quantify the reentrainment coefficient in the CMGBF penetration model.

Equation 10 with $\eta_R = 0$ was used to calculate the single dirty-granule collection coefficient, η_G, from the straight through penetration data in different particle size categories. The empirical collection coefficient, η_G, calculated in this fashion may contain the effects of simple air scouring, bounce, and reentrainment of particles unrelated to granular motion. On an overall mass penetration basis, simple air scouring of particles from the loaded, stationary bed was negligible.

The effective porosity of the bed ϵ, accounting for the intergranular dust deposit, was estimated from eq 13. For alumina granules, ρ_{bG} was found to be 1950 kg/m^3 by Happel's slow inversion technique (28). Loose bulk density of the fly ash, ρ_{bp}, was similarly measured as 900 kg/m^3.

With values of η_G, ϵ, and bed geometry, the single-granule reentrainment coefficient, η_R, was obtained from the CMGBF penetration model, eq 10, by using penetration data for the bed under normal operating conditions. Calculated values of η_R for the nine runs with alumina granules are presented in Table II. Calculated values of η_R range approximately from 0 to 10^{-7}. For this calculation, a negative value of η_R occurs when the penetration straight

Table II. Calculated Single-Granule Reentrainment Coefficient, η_R (Listed Values Are $\eta_R \times 10^8$)[a]

	particle diameter, μm (midpoint)					
run no.	0.08–0.23 (0.16)	0.23–0.46 (0.35)	0.46–0.91 (0.69)	0.91–1.83 (1.4)	1.83–3.66 (2.7)	3.66–7.31 (5.5)
1	1.31	−13.4	−2.50	3.64	1.46	11.4
2	9.61	−7.99	−21.3	2.63	30.7	58.3[b]
3	14.9	−8.01	9.73	28.7	24.7	91.6[b]
4	5.61	2.47	2.18	−8.46	18.8	19.5
5	2.15	−6.57	−4.56	3.66	19.9	52.7
6	47.3	3.97	80.9	88.3	82.9	37.9
7	49.1	22.0	18.6	82.1	49.0	45.8
8	22.3	15.5	8.73	40.9	58.0	20.7
9	0.0	−3.42	9.71	13.6	33.3	64.0
av	16.9	0.51	11.3	28.3	35.4	36.0
SE	6.4	3.9	9.5	11.8	8.1	7.4

[a] Conditions: $\epsilon_0 = 0.4$; ϵ = eq 3; $\rho_{bG} = 1950$ kg/m^3; $\rho_{bp} = 900$ kg/m^3; $d_G = 2.1$ mm (alumina). [b] Penetration straight through = 0, and η_R was estimated but not included in averages or regression.

through the stationary, loaded bed exceeds the penetrtion in the moving bed case. As shown in Table II, negative values occurred for small particles where measurement errors for the two penetration measurements overlap.

Table II shows the mean values of η_R as a function of particle size, again ignoring the effect of other variables. The reentrainment coefficient increases with particle diameter and appears to approach zero for particles roughly 0.3 μm in diameter. This approach to zero reentrainment is indicated in Table II by calculated zero or negative values of η_R in the submicron range.

The anomalously high value of η_R in the smallest particle size category in Table II suggests that particles less than 0.23 μm in diameter were reentrained, but this appears to be an artifact of the calculation procedure which assumes the difference between normal penetration and straight-through penetration is due solely to reentrainment.

Photomicrographs of particles reentrained from moving loaded beds, after dust feed had ceased, show a complete absence of very small particles approximately less than 0.3 μm. It is more likely that these small particles penetrate fissures or other flow paths in the moving bed under normal operating conditions and that these fissures quickly seal when bed motion ceases. Thus, actual straight-through penetration of these very small particles may have been underestimated during the stationary bed tests.

In addition to particle size, the effects on η_R of the intergranular dust deposit weight ratio, K, gas velocity, V_g, and granule velocity, V_G, were investigated by multiple regression. The resulting equation for prediction of η_R for moving alumina granules is

$$\eta_R = (-23.2 + 6.56 K d_p^{1/2} - 1.22[(V_g/100)^2 - 4]^2 + 849 V_G)/10^8 \quad (15)$$

where η_R = single-granule reentrainment coefficient (dimensionless), K = intergranular dust deposit weight ratio (percent by weight on granules), d_p = particle diameter (μm), V_g = superficial gas velocity (mm/s), V_G = granule velocity (mm/s). The squared multiple correlation coefficient, R^2, for eq 15, is 49%, and all coefficients except the intercept are highly significant ($P < 0.01$). Standarized residuals were approximately normally distributed.

The most significant term in 15 with respect to percent of variance explained is the product $K d_p^{1/2}$, indicating a positive interaction between K and $d_p^{1/2}$. Equation 15 tends to underpredict η_R at the highest K values, suggesting a stronger than linear trend with K, but the present data are insufficient to resolve a more complex form. Reentrainment increases with particle diameter but shows a trend more complex than the linear one suggested earlier by theoretical consideration of the ratio of simple air drag to adhesion forces.

The second term in eq 15 indicates a parabolic function for superficial gas velocity with reentrainment first increasing with gas velocity but then decreasing at the highest gas velocity. Run 1 suggests such a reduction in reentrainment at high gas velocity, which may be explained by greater removal of reentrained particles by subsequent impaction on other collectors.

Finally, granule velocity is seen to have a positive effect on reentrainment in the form of an incremental increase in η_R in the various particle sizes.

As defined here, reentrainment depends on granule motion. For a CMGBF with circumferential screen gas outlet, factors affecting intergranule shear at the wall should also strongly affect reentrainment; for example, increases in bed depth, granular bulk density, column diameter, and fluid pressure drop should all increase reentrainment. However, variations in these factors were not examined in the present study. A previous study demonstrated increased reentrainment with increased bed depth (13) as anticipated by this analysis. Equation 15, the regression equation describing reentrainment, considers the effect of other variables perhaps more closely related to resuspension of dust freed from granules by wall shear, rather than freeing of the dust from the granules in the first place.

These results show that reentrainment of collected dust strongly affects penetration in a CMGBF with a circumferential screen gas outlet as tested here. Alternate gas outlet designs such as that used by Rudnick and First (29) or one incorporating a sheath of clean granules at the gas exist zone that minimize the intergranular dust deposit and granule shear at the gas outlet should minimize reentrainment and reduce overall penetration appreciably.

Although the values of the single-granule reentrainment coefficient, η_R, predicted by eq 15 are specific for the CMGBF apparatus described previously, trends with operating variables should be generalizable to other granular bed designs. Also, the penetration model, eq 10, is applicable to other CMGBF configurations and should be useful in correlating experimental results.

Summary

A penetration model for aerosol filtration by a cocurrent moving bed of granules has been developed. The model incorporates straight-through penetration and reentrainment of previously collected dust due to granule motion, both mechanisms having been found to be significant in experiments. The model, an extension of classical clean-granular-bed theory, utilizes the familiar concept of a single-granule coefficient for collection and proposes a similar coefficient for reentrainment.

Experiments have confirmed the ability of the cocurrent moving granular bed filter to operate in a continuous mode and to enhance submicron particle filtration by the controlled formation of an intergranular dust deposit. Reentrainment was found to be a function of particle size and other factors such as gas velocity, granule velocity, and the extent of intergranular dust deposit. The single granule reentrainment coefficient, η_R, was found to depend upon the product of intergranular dust deposit and the square root of particle diameter ($K d_p^{1/2}$) for particle diameters between 0.16 and 5.5 μm.

Further experiments are needed to develop a predictive relationship for the single-granule reentrainment coefficient as a function of dimensionless groups in the manner of the classical single-granule collection coefficients. Trends concerning reentrainment due to granule motion identified in this work may also be useful for other practical collectors in which intergranular dust deposits preclude modeling by conventional clean bed theory.

Glossary

A	cross-sectional bed area perpendicular to gas and granule flow, m^2
C	particle concentration in gas stream, kg/m^3
C_i	particle concentration in gas stream inlet, kg/m^3
C_o	particle concentration in gas stream outlet, kg/m^3
D	bed diameter, m
K	mass ratio of dust in bed, % by wt
m	mass of collected dust in the differential volume, kg
N	number of gas parcels per second passing each granule, s^{-1}
Pt	$(C_o/C_i) \times 100$, %
Q_g	gas volumetric flow rate, m^3/s
Q_G	granule volumetric flow rate, m^3/s
V_g	superficial gas velocity, mm/s
V_G	granular velocity, mm/s
W_G	granular mass flow rate, g/min
Z	bed height, m
dZ	differential bed depth, m
d_G	granule diameter, m
d_p	particle diameter, μm
s_p	solidity of dust deposit, dimensionless
ϵ_o	clean-bed porosity, fraction
ϵ	loaded-bed porosity, fraction
ρ_p	particle density, kg/m^3
ρ_G	granule density, kg/m^3
ρ_{bG}	loose bulk density of granules, kg/m^3
ρ_{bp}	loose bulk density of dust, kg/m^3
η'_G	single-clean-granule collection coefficient, dimensionless
η_G	single-dirty-granule collection coefficient, dimensionless
η_R	single-dirty-granule reentrainment coefficient, dimensionless

μ internal coefficient of friction, dimensionless
μ' coefficient of friction at the wall, dimensionless

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Factors Affecting the Soluble–Suspended Distribution of Strontium-90 and Cesium-137 in Dardanelle Reservoir, Arkansas

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■ The variations of the concentrations of ^{90}Sr and ^{137}Cs at four stations in Dardanelle Reservoir were analyzed as functions of two parameters: concentration of ionic species and the activity released, A_r, from the two 900-MW reactors that use the reservoir as a source of cooling water. Multiple regression analyses were performed on the radionuclide concentrations by using the two parameters as predictors. The analyses indicated that ^{90}Sr is in a state of equilibrium between the solution and the suspended sediment. The position of the equilibrium was found to be quite sensitive to changes in the concentration of alkaline earth cations, M(II). Thus, the concentration of M(II) has a substantial effect on the removal of ^{90}Sr from the water column. The ^{137}Cs concentration varied as A_r, indicating that solution–sediment equilibrium has not been attained.

Introduction

The behavior of fission-produced radionuclides in the aquatic environment has been extensively studied since the time of the first nuclear weapons tests. Of great concern lately has been the interaction of dissolved radionuclides with clay minerals. This interaction is of great importance in the study of the fate of radionuclides released from power reactors and in studies of the geological storage of nuclear wastes. These studies can be classified according to the nature of the aqueous medium: solutions of high ionic strength containing relatively large amounts of radionuclides used in laboratory studies with processed clay minerals; marine and estuarine water; fresh water from lakes and rivers. In the latter two categories, the clay minerals are constituents of suspended or bottom sediments.

Laboratory studies of the distribution of ^{137}Cs and ^{90}Sr between solutions of high ionic strength and clay minerals, with an eye toward geological storage of nuclear waste, have been reviewed and described by Erickson (1) and Shiao et al. (2). It was found (2) that the distribution coefficient, D, of trace amounts of Sr(II) between a montmorillonite, pretreated to be completely of the Ca form, and a solution of Ca(II) could be expressed by the equation

$$\log D = -\log [\text{Ca(II)}] + k \qquad k = \text{constant} \qquad (1)$$

where [Ca(II)] was the concentration of Ca(II) in solution. The distribution coefficient for trace Cs(I) was expressed as

$$\log D = -0.5 \log [\text{Ca(II)}] + k' \qquad k' = \text{constant}$$

These relationships would be expected for either an ion-exchange or an adsorption equilibrium.

These phenomena can also be observed in natural waters. Noshkin and Bowen (3) have shown that while Pu appears to be removed from seawater by association with sinking particles, ^{137}Cs and ^{90}Sr remain in the water phase. Since some of these nuclides entered the marine environment associated with particulate matter, desorption due to increased ionic strength must be possible. The reversibility of the adsorption of ^{65}Zn and ^{54}Mn has been demonstrated by Evans and Cutshall (4). It was found that these nuclides were desorbed from suspended particles when the fresh water of the Columbia River was mixed with seawater in the river's estuary. The desorption of ^{65}Zn occurred from suspended particles but not from bottom sediment; on the other hand, ^{54}Mn was desorbed from both (5). In seawater, the large concentrations of species like Ca(II) force the equilibrium almost all the way to the side of the dissolved radionuclides; very little is left on the sediment.

Studies of the sediment–solution interaction in fresh water, using both reactor-produced and fallout radionuclides as tracers, have led to a better understanding of the means by which dissolved species are removed from a body of water. The major routes for the removal of radionuclides from lakes have been described by Lerman and Lietzke (6).

The route of most immediate interest in the study of ^{137}Cs and ^{90}Sr is adsorption by suspended and deposited sediment. In Lake Erie the most common mode of removal of ^{137}Cs is flux to the sediment, but sedimentation is a poor sink for ^{90}Sr. Lerman and Taniguchi (7) estimate that only 2–6% of the ^{90}Sr introduced into the Laurentian Great Lakes is removed by interaction with the sediment while sedimentation removes more than 80% of the ^{137}Cs. These findings have been confirmed by Alberts and Wahlgren (8) in their comparison of the 1976 and 1979 concentrations of these nuclides in these lakes. In the 20 years covered by these two studies, there has been little variation observed in the ^{90}Sr values. This is to be expected because the mean residence times in the Great Lakes range from 2.6 to 31 years. Thus no significant change in the concentrations of either fallout radionuclides or stable species such as Ca(II) would be expected. Even if an equilibrium had been established between dissolved and adsorbed species, it would be difficult to detect.

In contrast to the static conditions to be found in the Great Lakes and in seawater, the concentrations of ^{90}Sr, ^{137}Cs, and stable species in Dardanelle Reservoir, AR, vary widely over the period of a year. Dardanelle Reservoir, formed by the impoundment of the Arkansas River southwest of Russellville, has a volume of 486 200 acre feet. The montly flow through ranges from 200 000 to 20 000 000 acre feet except in periods of severe drought; thus, the mean residence time is usually less than 2 months and often on the order of weeks. The concentration of dissolved species can change quite rapidly; the total dissolved solids (TDS) ranges from 200 to 730 mg/L (9).

It will be shown that, in most samples, the major source of ^{90}Sr in Dardanelle Reservoir is fallout carried by the inflowing water. Only rarely is ^{90}Sr released from the two 900-MW reactors, operated by Arkansas Power and Light, which use the reservoir as a source of cooling water. Variations in the ^{90}Sr concentration should only be linked to the natural removal routes of the lake environment. Conversely, the bulk of the ^{137}Cs is reactor produced, and the variation in its concentration should be strongly linked to reactor releases and less strongly linked to the removal

processes if equilibrium is not rapidly achieved.

The study reported here is an analysis of the factors affecting the efficiency of the removal of ^{90}Sr from the water column and the factors controlling the amount of ^{137}Cs in the water column in Dardanelle Reservoir.

Methods

The concentrations of gross β activity, ^{90}Sr, ^{137}Cs, and TDS were measured monthly, with a few exceptions, from Jan 1976 to Aug 1977 and from May 1979 to July 1981. In the latter period, the concentrations of Na(I), K(I), and the combined Ca(II) + Mg(II), which will be referred to hereafter as M(II), were determined. The concentration of ^{90}Sr and ^{137}Cs on suspended sediments was determined in January, March, May, and July of 1981; the ^{90}Sr concentration on bottom sediments was determined in April of 1980 and 1981; ^{137}Cs was also determined on the latter date.

Samples of approximately 20-L volume were collected for radionuclide analysis, and 1-L samples were collected for analysis of gross β activity, TDS, and the cations. The samples were collected at four stations: (1) 400 m downstream from the reactor's cooling water discharge canal; (2) 400 m upstream from the reactor's cooling water intake; (3) 15 km upstream from the reactor facility; (4) 8 km downstream from the reactor facility at the Dardanelle Lock and Dam. The samples were taken from the surface since, at station 1, it was found that the heated water discharged from the facility remained in a surface layer 2 ft in depth.

The 20-L samples were acidified and filtered through Whatman 42 paper, Sr(II) and Cs(I) carriers (20–25 mg of cation) were added, and the sample was passed through a column containing ~100 g of Dowex-50 × 8, 100–200 mesh, at a rate of 1 L/h. The water passing through the column was discarded.

The cations were eluted from the column with 1 L of 6 N HCl. The eluate was evaporated to dryness, and the solids were redissolved in deionized water. The insoluble sulfide fraction was precipitated from basic solution by the addition of thioacetamide and saved for later processing. The insoluble carbonates were then precipitated and processed for the strontium fraction. The resulting decantate was processed to isolate the cesium fraction as a CsClO$_4$ precipitate from ethanol (10). The procedure for the purification of the strontium was essentially that of Hodges (11), except that the strontium was finally precipitated as SrSO$_4$. The final precipitates were filtered onto a paper disc, dried, weighed, mounted on a stainless steel planchet, and covered with a Mylar film of 1–4 mg/cm^2 thickness.

Gross β samples were obtained by evaporating 125–250 mL of filtered water. The solids were transferred quantitatively to cupped aluminum planchets and dried at 105 °C to constant weight and stored in a desiccator until counting. TDS was calculated from this weight.

The suspended solids were removed from the filter paper and leached of Sr(II) and Cs(I) by stirring for 2 h in 400 mL of 6 N HNO$_3$ spiked with stable Sr(II) and Cs(I) carriers. The slurry was filtered, and the filtrate was processed in the same manner as the eluate from the ion-exchange column described above.

Bottom sediments were collected from the upper 1 cm of the river bed by an Eckmann dredge. Only stations 1 and 3 were sampled since the bottom of the intake canal is scoured and the bottom at the dam is at such a depth as to make dredging very difficult.

The samples were dried at 105 °C and ground in a ball mill to pass a 40-mesh sieve. The fine mesh was necessary
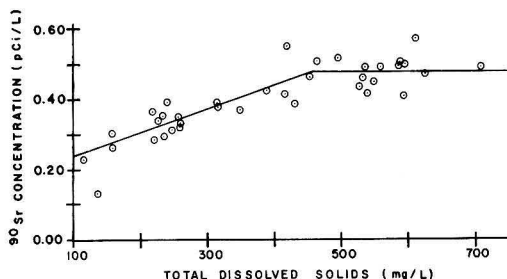
Figure 1. Concentration of ^{90}Sr as a function of total dissolved solids at station 1 (15, 16).

for the removal of shards of shell found in the sediment at station 1. A 40–70-g sample was slurried with 400 mL of 6 N HCl containing carriers and stirred for an hour. The slurry was filtered through two thicknesses of Whatman 42 paper. The solids were resuspended in 400 mL of 6 N HCl, stirred for another hour, and filtered. The combined filtrates were passed through ~100 g of Dowex 1 to remove Fe(III). The eluate was evaporated to dryness and processed as the eluate described above.

All samples were β counted in either a Tennelec LB-1000 low-background (0.97 cpm) counting system or a Tracerlab Omni-guard system (0.60 cpm background). Counting of the Sr fractions was delayed until at least 30 days after their separation to allow the ^{90}Sr–^{90}Y equilibrium to be reestablished. After correction for self-absorption and self-scattering (12) and for chemical yield, the activities of the samples were obtained from comparison with a standard.

The concentration of M(II) was determined by EDTA titration; concentrations of Na(I) and K(I) were determined by flame emission photometry (13).

All statistical computations were performed by using the packaged MINITAB routine (14) available on the University's Harris/7 computer.

Results and Discussion

The dependence of the ^{90}Sr concentration upon TDS in the water taken from station 1 (Figure 1) was first noticed when the complete body of data from the 1976–1977 period (15) was analyzed. The correlation coefficient for ^{90}Sr and TDS for TDS values less than 450 mg/L was ~0.75, a remarkably high value considering the number of parameters that could affect the ^{90}Sr concentration. At TDS values greater than 450 mg/L, the concentration was near constant 0.48 ± 0.04 pCi/L.

It is reasonable to expect that this relationship was due to the establishment of an ion-exchange type of equilibrium between aqueous ^{90}Sr and M(II) and these same species sorbed upon the surface of suspended sediment. If so, the data should be described by an equation derivable from ion-exchange theory. The distribution coefficient for Sr is

$$D_{Sr} \equiv \frac{(^{90}Sr)_c/\omega}{(^{90}Sr)/V} = \frac{[(^{90}Sr)_i - (^{90}Sr)]}{(^{90}Sr)} \frac{V}{\omega}$$

Since Sr^{2+} is a tracer component

$$D_{Sr} = a/M$$

where (^{90}Sr), $(^{90}Sr)_c$ = the equilibrium activity of ^{90}Sr in solution and on the solid, respectively (in pCi/L and pCi/kg), $(^{90}Sr)_i$ = the initial activity of ^{90}Sr in solution (in pCi/L), ω = the mass of ion-exchange medium (in kg), V

= the volume of solution (in liters; =1 L), M = the concentration of M(II) in the aqueous phase (in equiv/L), and a = constant. Rearranging these two equations into a linear form results in an equation amenable to linear regression analysis:

$$\frac{1}{^{90}Sr} = \frac{1}{(^{90}Sr)_i} + \frac{a}{(^{90}Sr)_i} \frac{\omega}{M} \quad (2)$$

It is assumed that $(^{90}Sr)_i$ is a constant, ~0.60 pCi, characteristic of fallout and runoff in this watershed. This is the activity observed when M(II) concentration is greater than 2.5 mequiv/L, at which time the amount of ^{90}Sr associated with the sediment is small compared to that in solution.

It must be pointed out that the term ω represents not the concentration of suspended sediment at the time of sample collection but rather the total amount of clay that has been available for ion exchange along the whole course of the Arkansas River and thus should be considered a constant. This is borne out by statistical analysis, which indicates that the amount of suspended material present at any single time is not an effective predictor of the aqueous ^{90}Sr concentration. If ω is considered to be a constant, equation 2 can be simplified:

$$1/^{90}Sr = 1/C_1 + C_2/M \quad (3)$$

where $C_1 = (^{90}Sr)_i$ and $C_2 = a\omega/(^{90}Sr)_i$.

If ion-exchange equilibrium controls the concentration of ^{90}Sr in Dardanelle Reservoir water, the data should fit eq 3 well. The concentrations of ^{90}Sr and M(II) in samples from each station are presented in Table I.

Since newly injected ^{90}Sr would disturb the equilibrium between solution and sediment, it must be certain that there is no significant amount of reactor-produced ^{90}Sr present in the samples. If there is little difference between samples taken from station 2 (immediately before the water passes through the reactor's cooling system) and from station 1 (immediately after the water has been released from the cooling system), it may be assumed that the amount of "new" ^{90}Sr is negligible. Samples in which this difference is 0.07 pCi/L or greater have been discarded with one exception noted in Table I. This cutoff value was chosen because it is twice the relative error in the values for ^{90}Sr concentration.

That the bulk of the aqueous ^{90}Sr has been present in the Arkansas River for sufficient time to establish equilibrium with suspended sediments is indicated by its presence in predictable quantities in the Ozark Dam impoundment, approximately 55 km upstream. In Nov 1980, a control sample taken at Ozark Dam had a ^{90}Sr concentration of 0.56 pCi/L compared to a value of 0.50 pCi/L in Dardanelle Reservoir, indicating also that the main source of ^{90}Sr is fallout rather than release from the reactors.

A plot of the inverse of the ^{90}Sr concentration as a function of the inverse of M(II) concentration for samples from station 1 is presented in Figure 2. The "goodness of fit" of the data to eq 3 is measured by the R^2 value calculated by the linear regression subprogram of the MINITAB package. R^2 is the percentage of variance in $(^{90}Sr)^{-1}$ that can be predicted from the parameters chosen as predictors. In this case, the only measured parameter that was significant as a predictor was M^{-1}; R^2 is thus simply the square of the correlation coefficient, r, of these two variables multiplied by 100.

Table II is a tabulation of the values for the constants C_1 and C_2 and the R^2 and r values for the regression lines for each individual station. The fit of station 1 data to eq

Table I. Concentrations of ^{90}Sr (pCi/L) and M(II) (mequiv/L) in Water Samples Taken from Dardanelle Reservoir

	station 1		station 2		station 3		station 4	
date	^{90}Sr	M(II)	^{90}Sr	M(II)	^{90}Sr	M(II)	^{90}Sr	M(II)
5/79	0.34	1.00	0.31	0.80	0.40[c]	1.05	0.54	2.20
8/79	0.55[a]	2.05	0.48	2.05	0.50	2.95	0.49	2.80
10/79	0.57[a]	2.80	0.50	3.00	0.50	3.15	0.49	2.90
11/79	0.51	2.85	0.48	2.90	0.42	3.05	0.64	3.10
12/79	0.50	2.35	0.43⁵	2.35	0.42	2.30	0.39	2.35
1/80	0.35	1.35	0.29	1.35	0.39	1.95	0.35	1.80
2/80	0.39	1.80	0.36	2.00	0.45	2.55	0.49	2.50
3/80	0.45[b]	2.25	0.38	2.65	0.45	3.20	0.43	2.90
4/80	0.37	1.65	0.35	1.65	0.33	2.50	0.46	2.45
5/80	0.50	2.45	0.45	2.35	0.43	2.15	0.49	2.00
7/80	0.41	3.05	0.42	3.05	0.54	3.75	0.48	3.35
8/80	0.50	3.35	0.50	3.30	0.46	3.50	0.47	3.55
9/80	0.51	3.45	0.51	3.40	0.48	3.30	0.48	3.45
10/80	0.50	3.40	0.49	3.40	0.50	3.40	0.47	3.40
11/80	0.49	3.25	0.51	3.20	0.48	3.30	0.50	3.30
12/80	0.50	3.30	0.50	3.20	0.48	3.20	0.50	3.35
1/81	0.50	3.15	0.45	3.10	0.44	2.90	0.46	3.05
2/81	0.46	3.00	0.43	3.00	0.42	2.35	0.43	3.00
3/81	0.39	2.05	0.38	1.95	0.35	1.90	0.35	2.10
4/81	0.38	1.35	0.42	1.35	0.37	1.85	0.46	1.55
5/81	0.30	1.55	0.24	1.45	0.52[c]	2.05	0.38	1.95
7/81	0.45	2.90	0.42	2.80	0.42	3.10	0.43	2.95

[a] Value discarded because it is ⩾0.07 pCi/L greater than station 2 value. [b] Value not discarded because station 2 value is suspect. [c] Value discarded because of statistically large variance.

Table II. Constants for Eq 3, R^2 Resulting from Multiple Regression, and r for $(^{90}$Sr$)^{-1}$ and M^{-1}

station	C_1, pCi/L	C_2, mequiv L/pCi	R^2	r
1	0.64 ± 0.05	1.67 ± 0.26	69.3	0.83
2	0.60 ± 0.07	1.67 ± 0.40	47.2	0.69
3	0.76 ± 0.12	2.62 ± 0.55	55.9	0.75
4	0.81 ± 0.15	2.59 ± 0.57	51.1	0.71

3 is very good; the r value being 0.83. This value is remarkably close to the value expected of data obtained from experiments in which extraneous variables are well controlled (0.95). The fit at the other three stations is not quite so good, but the r values are all in the area of 0.7.

The statistical fit for data at station 1 is much better than for data for the same water at station 2, even though the constants are virtually the same. The water at station 2 has recently been diluted to a small extent by water from a minor tributary of the Arkansas River, the Illinois Bayou, which may slightly stress the equilibrium. As the water is released from the the cooling system, it flows turbulently through the discharge canal, whose bottom is almost wholly red clay that is relatively rich in sorbed ^{90}Sr. By the time the water reaches station 1, equilibrium may well be reestablished. Station 4 water is also diluted to some extent by the Illinois Bayou.

That the data fit eq 3 well is no great surprise. This type of behavior has been observed in studies of soils and processed clays, but it has not been observable in most natural bodies of water because it is rare for a body of water to exhibit a variation in the M(II) concentration from 1.0 to 3.5 mequiv/L in so short a time as a year. Only because of this rapid change in equilibrium conditions does this equilibrium become evident in the Arkansas River.

The concentration of ^{90}Sr in suspended sediments should exhibit an inverse relationship to the concentration of M(II) in solution. There are indications of such a trend, summarized in Table III. The uncertainty in the ^{90}Sr values is large because the samples were small, as little as 0.18 g, and the count rate for the Sr fraction was only slightly above background. In Jan 1981, the samples were so small that they were combined for a single analysis.
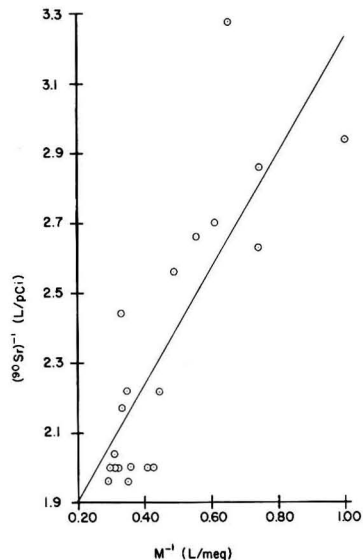
Figure 2. Dependence of ^{90}Sr activity upon M(II) concentration: station 1.

Consequently, a weighted average for each month is also included in Table III. These averages indicate that there is an inverse relationship between sorbed ^{90}Sr and aqueous M(II).

The distribution coefficient for ^{90}Sr(II) has values of 250–500 L/kg in the 4 months in which both the water and the filtered solids were analyzed. This is in the range of the value obtained by extrapolating the data of Shiao et al. (2) for Sr(II) sorbed on the calcium form of montmorillonite.

Of interest also is the comparison of the ^{90}Sr on suspended matter and that on bottom sediments (Table III). The bottom sediments are somewhat higher in ^{90}Sr than the suspended material. No conclusion, as yet, can be

Table III. Concentrations of ^{90}Sr (pCi/g) in Sediments as Function of Aqueous M(II) Concentration (mequiv/L)

| type of sediment | date | species | station | | | | | |
			1	2	3	4	combined sample	
suspended	7/81	^{90}Sr	0.14 ± 0.11	0.20 ± 0.20	0.00 ± 0.15	0.14 ± 0.18	0.12 ± 0.10	
		M(II)(aq)	2.88	2.81	3.11	2.93	2.93	
suspended	5/81	^{90}Sr	0.24 ± 0.07	0.18 ± 0.07	0.10 ± 0.03	0.14 ± 0.09	0.21 ± 0.07[a]	0.11 ± 0.07[b]
		M(II)(aq)	1.58	1.46	2.04	1.95	1.52	2.00
suspended	3/81	^{90}Sr	0.15 ± 0.12	0.16 ± 0.10	0.08 ± 0.06	0.09 ± 0.09	0.11 ± 0.05	
		M(II)(aq)	2.03	1.94	1.88	2.11	1.99	
suspended	1/81	^{90}Sr					0.10 ± 0.04	
		M(II)(aq)					3.04	
bottom	3/81	^{90}Sr	0.32 ± 0.04		0.34 ± 0.04			

[a] Stations 1 and 2 combined. [b] Stations 3 and 4 combined.

drawn as to the mechanism by which the bottom sediment has acquired the added load of ^{90}Sr.

The case of ^{137}Cs is quite different. There is usually a significant amount of this nuclide released from the reactors. Since the distribution coefficient for Cs$^+$ is quite large, the equilibrium concentration of ^{137}Cs in the reservoir would be expected to be quite low, much smaller than the quantities released from the reactor. Thus, at the downstream stations, the concentration of ^{137}Cs should be dependent principally upon the total activity released from the reactors, A_r, with only a small contribution from other sources:

$$[^{137}\text{Cs}] = C_3A_r + A_i \qquad (4)$$

where [^{137}Cs] = the concentration of ^{137}Cs (in pCi/L), A_i = the activity of ^{137}Cs not contributed by the reactors ($\sim C_4$(TDS) ≪ C_3A_r for this study), and C_3, C_4 = constants.

The variable A_r was calculated from the empirical relationship between gross β activity and TDS (15, 16) since part of the data used was gathered before potassium analysis was begun:

$$A_r = (\text{gross } \beta \text{ activity}) - 0.0108(\text{TDS}) \qquad (5)$$

The latter term includes the activities of ^{90}Sr–^{90}Y and the naturally occurring nuclides, principally ^{40}K.

The values of the parameters used in eq 4 and 5 are tabulated in earlier works (15, 16). It is of interest to note that samples from all stations contain reactor-produced activity, even the upstream stations. This is to be expected at station 2. A hydrological model investigation by Bechtel Corp. (17) indicated that a circulation pattern would be established between outlet and inlet as a result of the pumping of cooling water. Reactor-produced nuclides, initially airborne, find their way even to station 4 (16).

Linear regression analyses showed that the only significant predictor of the ^{137}Cs concentration was A_r (Table IV) and that the other term in eq 5, whether it is dependent on TDS or not, does not significantly add to the total R^2 for the equation. It must be concluded that nowhere in the reservoir is the ^{137}Cs approaching an equilibrium between sorbed and dissolved species.

It is interesting to note the change in the value for C_3 as the distance from the reactor increases and/or the concentration of gross β activity decreases. C_3 is the fraction of the total activity released that is ^{137}Cs. This fraction decreases with time since release, indicating that there is some selective removal mechanism for ^{137}Cs other than dilution at work in Dardanelle Reservoir. It is impossible to pinpoint the mechanism(s) responsible for this removal from the available data. It is doubtful that the only mechanism is an ion-exchange type of process. The observed D value ranges from 10^4 to 10^5 L/kg at stations 1, 2, and 4, much higher than the value of $\sim 10^3$ (the value observed at station 3) predicted by Shiao et al. (2). This

Table IV. Constants for Eq 5 and R^2 Resulting from Multiple Regression Analysis of Aqueous ^{137}Cs Concentrations

| station | C_4 | C_3 | R^2, % | | |
			due to TDS	due to A_r	total
1	−0.428 ± 0.124	0.188 ± 0.018	5.6	77.6	83.2
2	0.122 ± 0.041	0.0292 ± 0.0097	7.7	62.3	70.0
3	0.0842 ± 0.0441	0.0156 ± 0.0107	4.8	56.0	60.8
4	0.0	0.0552 ± 0.0258	0.0	40.7	40.7

is consistent with the findings of Duursma (18) that there is little exchange of ^{137}Cs with stable Cs in some marine sediments.

In any case, it is certain that equilibrium between ^{137}Cs in solution and in the sediment has not been reached prior to the time the water leaves the reservoir in periods of normal flow. The concentration of the newly injected nuclide remaining unprecipitated is greater than the equilibrium concentration because the time necessary to establish equilibrium between solution and sediment is significantly longer than the normal mean residence time of the water in Dardanelle Reservoir.

In the Arkansas River, with its considerable load of suspended sediment, fallout ^{90}Sr(II) has resided long enough in the water to have attained equilibrium with the suspended solid via an exchange process involving the surface of the suspended matter and a solution containing M(II) and ^{90}Sr(II). The equilibrium concentration of ^{90}Sr is quite sensitive to changes in the concentration of M(II) as long as the concentration is less than 2.5 mequiv/L. There is no doubt that the concentration of alkaline earth cations can significantly affect the efficiency of the removal (by flux to the sediment) of ^{90}Sr from the fresh water column.

No conclusion can be reached about the effect of dissolved species on the ^{137}Cs concentration because equilibrium conditions do not exist in Dardanelle Reservoir since the reactor facility is a constant source of this radionuclide. Studies of ^{137}Cs much further downstream from Arkansas Nuclear One will be necessary for a study of equilibrium conditions.

Acknowledgments

Registry No. ⁹⁰Sr, 10098-97-2; ¹³⁷Cs, 10045-97-3.

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Mutagenicity and Chemical Characteristics of Carbonaceous Particulate Matter from Vehicles on the Road

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■ Experiments were conducted in the Allegheny Mountain Tunnel of the Pennsylvania Turnpike in 1979 to evaluate bacterial mutagenicities of particulate emissions from heavy-duty diesels and gasoline-powered vehicles in highway operation. Filter samples were extracted with dichloromethane followed by acetonitrile. Ames assays with and without microsomal activation, HPLC fluorescence profiles, GC molecular weight distributions, and particle size distributions were obtained. We find that (1) the diesel particulate matter at Allegheny resembles that encountered in dilution-tube studies by all criteria studied (particulate mass emission rate, extractability, particle size, extract HPLC profile, extract molecular weight distribution, and mutagenicity—though these findings do not preclude the possibility of substantial differences in *detailed* chemical properties), (2) in revertants per microgram of dichloromethane-extracted material at Allegheny, the mutagenicities of the diesel particulate matter and of the local rural ambient particulate matter are of the same order of magnitude, and (3) in revertants per kilometer traveled, the mutagenicity of particulate emissions from heavy-duty diesels is several times (median ~6 times) that of emissions from gasoline-powered vehicles.

Introduction

The prospect of widespread diesel automobile use, together with the 1977 report (*1*) that diesel exhaust par-

ticulate matter is mutagenic as measured by the *Salmonella typhimurium* plate incorporation assay (Ames test (*2*)), has set in motion a large effort, here and abroad, to evaluate the mutagenicity and potential human carcinogenicity of diesel exhaust particulate emissions. A serious obstacle to a realistic evaluation is that most of the existing information derives from laboratory dynamometer/dilution-tube measurements. For reasons having to do with dilution ratio, residence time, opportunity (or lack thereof) for interaction with atmospheric gases and particles or with other exhausts, vehicle operating practices (upkeep, driving patterns), and many other factors, the relevance of dynamometer/dilution-tube measurements to the actual environment inevitably comes under question. There have been, or are now in progress, only a few experiments (*3–8*) that have any bearing on the latter issue, even in a near-to-the-road setting.

The present experiments were conducted at the Allegheny Mountain Tunnel of the Pennsylvania Turnpike in 1979 to evaluate the mutagenicity and general chemical properties of diesel particulate organic material in a realistic near-road environment. Characteristic of the experimental setting are residence times of a few minutes (0–6, average 2.5) and exhaust dilution ratios ≈10³–10⁴, with no exposure of the exhaust to sunlight. We seek to know:

(1) Are the Ames-assay mutagenicities and chemical properties of diesel particulate emissions similar on-road to those reported (*5, 9–31*) in dynamometer/dilution-tube experiments?

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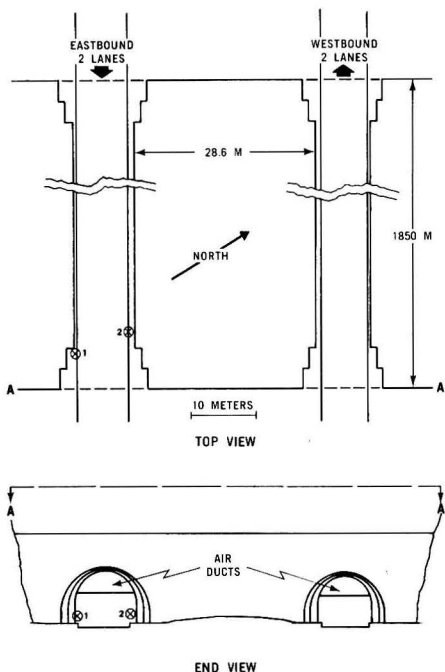
Figure 1. Allegheny Mountain Tunnel. Crosses indicated east portal sampling locations in eastbound tunnel (1 = right side, 2 = left side). Overhead air ducts for ventilation intake air are indicated on the end view.

Figure 2. Visual counts of eastbound traffic through the Allegheny Mountain Tunnel during the Aug/Sept 1979 experiment: upper = spark-ignition vehicles; lower = diesel vehicles.

(2) How does the Ames-assay mutagenicity of exhaust particulate material from on-road diesels compare with the mutagenicity of exhaust particulate matter from on-road spark-ignition vehicles?

(3) How does the Ames-assay mutagenicity of exhaust particulate material from on-road diesels compare with ambient-aerosol mutagenicity?

The criteria for comparison between on-road and dilution-tube samples are mass emission rates, extractability (mass percent) by Soxhlet extraction into dichloromethane (CH_2Cl_2), particle size distribution, high-performance liquid chromatography (HPLC) profiles, gas chromatographic (GC) molecular weight distributions (more properly, boiling point distributions), and Ames-assay mutagenicities. Mutagenicities of diesel and spark-ignition emissions are compared on a revertants-per-kilometer basis and on a revertants-per-extractable-mass basis. Mutagenicities of diesel particulate matter (or the particulate matter from traffic undifferentiated as to vehicle type) and the local ambient aerosol are compared on a revertants-per-extractable-mass basis.

Experimental Section

There were two field experiments in this study, namely, May 25 through June 1, 1979, and Aug 25 through Sept 7, 1979. Both were at the Allegheny Mountain Tunnel of the Pennsylvania Turnpike.

Sampling Site. Allegheny Tunnel is a four-lane dual tunnel 1850 m long, running approximately east–west (two eastbound lanes in one tunnel, two westbound lands in the other; see Figure 1) through Allegheny Mountain in southwestern Pennsylvania at an altitude of 707 m above sea level. The roadbed is essentially straight, with a net grade 0.5% downward toward the east. Traffic conditions

are representative of highway cruise, at speeds close to the posted 55 mile/h limit. All tunnel air sampling was conducted in the eastbound tunnel.

Strong diurnal and weekly traffic patterns (Figure 2) permit sampling in periods dominated by diesels and periods dominated by spark-ignition vehicles. Traffic composition was determined by visual count. Traffic volume was determined by a road-tube recording axle counter in combination with the visual counting.

The traffic composition eastbound for a given sampling period ($\sim$12 h) ranged from 31% to 93% spark-ignition in the two experiments. Of the spark-ignition vehicles, 98% were light duty (passenger cars, motorcycles, pickup trucks, recreational vehicles). The diesels were predominantly heavy-duty trucks (average $\sim$30 tons, according to Turnpike records). Diesel automobiles comprised 2.4 ± 0.5% of the automobile traffic. Heavy-duty spark-ignition vehicles comprised 6% of the heavy-duty traffic (1.5% of all traffic).

The tunnel sampling stations were located 3.4–8.5 m in from the east (exit) portal, 1.8–2.2 m above road level, and 0.45–0.8 m away from the edge of the road on each side, as signified with crosses in Figure 1. Because of the piston effect of the traffic, reinforced by the prevailing wind from the west, all of the air outflow from the eastbound tunnel is through the east portal, at flow rates $\sim$20 000 m^3/min as monitored by a Gill anemometer situated 47 m inside the east portal. Accordingly, the tunnel sampling stations registered the cumulative emissions for the whole length of the tunnel. These emissions include not only the exhaust emissions but such things as entrained road dirt, tire-wear particles, etc.

Approximately 40% of the air going into the eastbound tunnel during these experiments entered through the west (entrance) portal under the influence of the traffic piston effect and the prevailing wind. The rest of the inflow was split equally between the west and east sets of ventilation intake fans on the two sides of the mountain, the air entering the tunnel via overhead louvers (see Figure 1). For sampling the air coming into the tunnel, stations were set up in the east and west fan rooms. It should be recognized that the emission-rate calculations require using the composition of the incoming air, which is slightly contaminated by Turnpike traffic emissions; the relatively clean rural air farther away is not representative of the air entering the tunnel.

In the Aug–Sept experiment, air was sampled also at the top of an abandoned 16-m-high radio tower on the mountaintop (elevation 838 m at the foot of the tower) to provide material representing local rural ambient air.

General Approach. The underlying concept of the experiments is described in other publications (32–37).
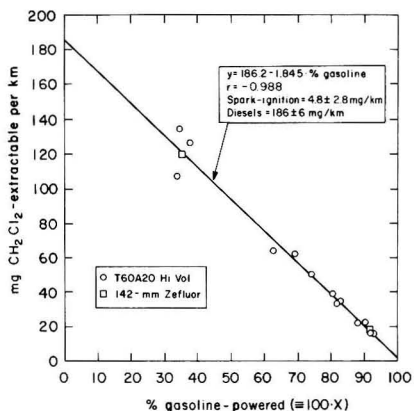
Figure 3. Plot of mg/km emission rate of CH_2Cl_2-extractable particulate matter vs. traffic composition, Allegheny Mountain Tunnel Aug/Sept 1979 experiment. Intercept at 0% spark-ignition vehicles is the emission rate (186 ± 6 mg/km) from diesels; for spark-ignition vehicle estimate, see explanation in text.

One samples simultaneously the tunnel air and the incoming ventilation air and obtains by difference the vehicle contribution to any given constituent in the tunnel air. Meanwhile one determines the traffic count and tunnel air flow so that the emission rate of any component can be ascertained:

$$E = \Delta \cdot V/T \qquad (1)$$

where E is the emission rate ($\mu g/km$) averaged over all vehicles, Δ is the concentration difference ($\mu g/m^3$) between tunnel and incoming air, V is the total volume of air (m^3) through the tunnel, and T is the total kilometers driven, i.e., the product of the number of vehicles and the tunnel length (1.85 km). Also, for the ith sampling period the emission rate E of any constituent can be written

$$E_i = x_i G + (1 - x_i)D \qquad (2)$$

where G is the spark-ignition-vehicle average emission rate ($\mu g/km$), D is the diesel-vehicle average emission rate ($\mu g/km$), and x_i is the quotient of the number of spark-ignition vehicles and the total number of vehicles in the ith run, i.e., percent spark-ignition vehicles /100. Equation 2 can be rewritten

$$E_i = (G - D)x_i + D \qquad (3)$$

Thus for a series of sampling runs ($i = 1, 2, \ldots$), the plot of E vs. x is linear with intercepts

$$
\begin{aligned}
E = D & \quad x = 0 \\
E = G & \quad x = 1
\end{aligned}
\qquad (4)
$$

In this manner, $\mu g/km$ emission rates can be derived for the two main vehicle categories separately, by linear least-squares regression. Figure 3 illustrates the procedure with use of emission rates of CH_2Cl_2-extractable particulate matter as the example.

The derivation of eq 4 presupposes that there are no light-duty diesels so that values of unity for x are achievable and D is independent of x. But as noted above, in the 1979 experiments 2.4% of the automobiles were diesels. This means that x cannot exceed 0.976 and that D decreases as x increases because of an increasing ratio between light- and heavy-duty diesels. Accordingly, G is calculated from the value of E at $x = 0.976$ by the expression

$$G = (E_{0.976} - 0.024DR)/0.976 \qquad (5)$$

where R is the ratio between light- and heavy-duty diesel emissions rates, taken in the present analysis to be $^1/_3$ on the basis of fuel-economy estimates (based, for example, on ref 38 for heavy-duty diesels). This correction is important because the particulate emission rate of a diesel car is many times that of the average spark-ignition car. (Actually, G is not quite independent of x, because at low x more of the spark-ignition vehicles are heavy duty. This refinement is inconsequential because heavy-duty spark-ignition vehicles were <2% of the traffic, and their contribution to the heavy-duty particulate emissions is only a few percent.)

Sampling Apparatus and Procedures. Samples were collected, in ~12-h periods, concurrently at four stations—east portal right side, east portal left side, east fan room, west fan room—on preweighed 8 in. × 10 in. Pallflex T60A20 Teflon-impregnated glass fiber HiVol filters. The HiVol units were equipped with flow controllers and were fitted with cyclone preseparators (nominal cutoff diameter 5.5 μm) to exclude large particles and, more important, to exclude light.

The HiVol start and stop times were chosen in accordance with the traffic composition (Figure 2) to discriminate as much as possible one vehicle category from the other. Immediately after sampling, the filters were folded, wrapped with aluminum foil, and stored in manilla envelopes over dry ice (−78.5 °C) in the dark until time for weighing and extraction.

Because of concern about chemical inertness and collection efficiency of the T60A20 medium, samples were collected also on 142-mm diameter pure Teflon membrane filters of 0.2-μm nominal mean pore diameter (Ghia Corp. Zefluor filters). Owing to the flow-rate penalty of these filters, long sampling periods (e.g., 25 h) were required. Each 142-mm filter sampler inlet was fitted with a dichotomous sampler head (39) to exclude large particles and light. Flow was held constant at ~60 L/min by means of a vacuum regulator at the inlet of each pump. The pumps were of metal bellows construction, which is inherently free of leakage paths to the outside. Flow was measured by a calibrated temperature-compensated dry gas displacement meter at the pump outlet. After sampling, the 142-mm filters were handled in the same manner as the HiVol filters.

In the Aug/Sept experiment, a long-term (124 h) T60A20 HiVol was operated in the west fan room. The tower sampling was also long-term (144 h), approximately at the same time as the west fan room long-term collection. A 142-mm Zefluor filter was used at the tower.

Particle size distributions were obtained at east portal and west fan room stations in the Aug/Sept experiment by use of modified eight-stage 1-ft^3/min Andersen cascade impactors with after filters. The impactor collection stages were polyethylene and the after filter was quartz fiber (Pallflex Tissuquartz 2500 QAO).

There was no attempt to control the sampling temperature. Average ambient temperature at the Altoona/Martinsburg National Weather Service Station was 12.5 °C in the May/June experiment and 20.5 °C in the Aug/Sept experiment.

Sample Weighing and Extraction. Mass determinations were carried out under subdued yellow light at 22 °C and 50% relative humidity after the filters or impactor stages had reached constant weight in the dark. Particulate mass was obtained by difference, with control filters and stages to cancel any tare weight changes between weighings before and after sampling.

Table I. Ford and EPA/RTP HPLC Procedures and Chromatogram Nomenclatures

expt(s)	EPA/RTP	Ford method no. 1	Ford method no. 2[a]
sample injection solvent	May/June and Aug/Sept CH_2Cl_2	May/June and Aug/Sept CH_2Cl_2 or CH_3CN[b]	Aug/Sept only $CHCl_3$ + trace toluene[c]
column	25-cm stainless steel	radial compression[d]	radial compression[d]
detection			
excitation λ, nm	313	280	280
emission λ, nm range (filter)	≥418	≥389	≥418
flow rate, mL/min	1	2	2
elution program			
initial	5% CH_2Cl_2 in hexane for 15 min	n-heptane for 0 min	n-hexane for 0 min
gradients and steps	to CH_2Cl_2 (at 5%/min), CH_2Cl_2 for 21 min	to $CHCl_3$ in 10 min, $CHCl_3$ for 6 min, CH_3CN step (10 min)[e]	to CH_2Cl_2 in 20 min, CH_2Cl_2 for 6 min, CH_3CN step (10 min)
reverse gradients and steps	to 5% CH_2Cl_2 in hexane (at 10%/min)	$CHCl_3$ step (6 min), n-heptane step (15 min)	CH_2Cl_2 step (10 min), to n-hexane in 20 min
analysis time, min	55	26	36
cycle time, min	70	47	75
peak quantitation	height and planimetry	electronic integration	electronic integration
peak designations			
aromatics	$\alpha(\alpha_1, \alpha_2)$	PAH-1,2,3	PAH-1,2,3,4
slightly polar	β	TRANSITION-1,2,3	PAH-5
moderately polar	$\gamma(\gamma_1, \gamma_2)$	TRANSITION-1,2,3	TRANSITION-1,2,3,4
polar	δ	OXYGENATES	OXYGENATES

[a] See p 97 of ref 22. [b] CH_2Cl_2 for dried CH_2Cl_2 extracts, CH_3CN for dried CH_3CN extracts. [c] Toluene added as an internal standard. [d] Waters Associates, Inc. [e] Solvent was switched from 100% $CHCl_3$ to 100% CH_3CN, which then continued for 10 min.

After weighing, the filter samples were allocated between Ford and EPA/RTP—for extraction and chemical analysis at Ford and for extraction, chemical analysis, and Ames testing at EPA/RTP. All filter samples were initially extracted in a Soxhlet apparatus for 12–18 h with CH_2Cl_2. At Ford the thimble chamber was heated by a hot vapor jacket during extraction. Each extract was filtered through a Teflon membrane filter of 0.2-μm nominal pore diameter (Ghia Corp. Zefluor at Ford, Millipore Corp. Fluoropore at EPA/RTP) and concentrated in a rotary evaporator under vacuum. Evaporation to dryness was completed under a nitrogen stream without applied heat. The dried and dissolved extracts were stored over dry ice (Ford) or in a 20 °C freezer (EPA/RTP) in the dark. Chemical analyses and Ames assays were performed on all CH_2Cl_2 extracts.

Some of the filters were further extracted in acetonitrile (CH_3CN). A few of the filters after CH_3CN extraction were further extracted with o-dichlorobenzene (o-Cl_2Ph) in a stream of oxygen. Chemical analyses and Ames assays were conducted on a few of the CH_3CN extracts.

Particle Size Distribution. The mass on each impactor stage and on the after filter was converted to μg/m^3. The resulting tunnel values were corrected for the corresponding intake fan room values to yield a size distribution for the vehicle-associated particulate matter.

HPLC Procedures. Samples of dried CH_2Cl_2 and CH_3CN extracts were redissolved and analyzed by normal-phase HPLC on silica gel by using gradient elution with fluorescence detection. There were three procedures, as spelled out in Table I.

HPLC fluorescence peaks were quantified by peak area or peak height (Table I), which, normalized for the fraction of the parent sample represented by the sample injected, were reexpressed as areas or heights per kilometer driven. Regression vs. traffic composition then yielded the fluorescence-intensity ratio for, say, TRANS-1, between diesel and spark-ignition vehicles.

Molecular Weight Distributions. Molecular weight distributions were determined on CH_2Cl_2 extracts by using the GC procedure described by Black and High (40). The

micrograms-per-cubic-meter value in the tunnel at each carbon number was corrected for the intake-air concentration (always very low). The net micrograms per cubic meter at each carbon number was converted to a milligrams-per-kilometer emission rate, which in turn could be treated by linear regression against traffic composition to obtain milligrams-per-kilometer emission rates for each of the two vehicle categories at the carbon number in question. The process was repeated at each carbon number to construct a GC molecular weight distribution for diesels alone and for spark-ignition vehicles alone.

Ames Mutagenicity Assays. The dried extracts were taken up in dimethyl sulfoxide, and *Salmonella typhimurium* dose/response curves were generated as described elsewhere (28). The slope of the linear part of each dose/response curve was calculated by least-squares linear regression, including always the data point at zero dose and excluding only those high-dosage points that, when plotted, were obviously below the initial straight line.

The slope values were converted to total revertant colonies per filter by multiplying by extractable sample mass. These results were corrected for blank-filter mutagenicity. The net was divided by the air volume sampled to yield the mutagenicity on a revertants-per-cubic-meter basis. The difference in revertants per cubic meter between the tunnel and the fan rooms is the activity in the tunnel that is attributable to vehicles alone. This difference is analogous to Δ (μg/m^3) in eq 1 and is entered in eq 1 to obtain, for the given sampling run, the number of revertants per kilometer driven. The revertants per kilometer values are treated by linear regression against traffic composition (eq 2–5) to yield a value of revertants per kilometer for heavy-duty diesels and another for spark-ignition vehicles.

Since the micrograms of extractable material per vehicle-kilometer for each vehicle category has similarly been determined as earlier described (see Figure 3), the revertants-per-kilometer values can be divided by their respective microgram-per-kilogram values to yield revertants per microgram of extractable material for each vehicle category. Finally, the intake-corrected tunnel revertants

Table II. Emissions of Total and Extractable Particulate Mass (mg/km and % of Total), Allegheny Tunnel, 1979

	spark-ignition vehicles		diesel trucks[a]	
	May/June	Aug/Sept	May/June	Aug/Sept
CH_2Cl_2 extractable	12 ± 3^b ($\sim40\%$)[c]	5 ± 3^d	192 ± 6 (26%)[e]	186 ± 6 (22%)[e]
CH_3CN extractable after CH_2Cl_2	f	1 ± 1^d	f	11 ± 3 (1%)[e]
o-Cl_2Ph extractable after CH_3CN	~0 ($\sim0\%$)[c]	g	0 (<9) ($\leqslant1\%$)[e]	g
total particulates	30 ± 11	6^{+11}_{-6}	751 ± 20	860 ± 22

[a] Average gross weight approximately 30 tons. [b] Error quoted is the standard deviation (σ). [c] Percent of the total particulate mass from spark-ignition vehicles. [d] Percent is not stated because of large error limits. [e] Percent of the total particulate mass from diesel trucks. [f] Poor agreement in May/June HiVol and Zefluor CH_3CN results, and only two sample sets of each filter type were analyzed by CH_3CN extraction. [g] No o-Cl_2Ph extraction was conducted.

total for the whole experiment is divided by the intake-corrected tunnel mass of extractable material to obtain an overall average revertants per microgram for traffic.

On the May/June HiVol samples, five tester strains—TA98, TA100, TA1535, TA1537, TA1538—were used, with and without S9 activation, generally in triplicate at each dose, on pooled CH_2Cl_2 extracts of T60A20 filters. Samples were pooled in order to provide enough material to test with all five strains. For the tunnel samples, samples from periods of mainly diesel traffic went into one pool and samples from periods of mainly spark-ignition traffic went into the other. All available fan-room HiVol extracts were combined into one pool.

On the May/June 142-mm membrane filter samples, only TA98 was used, with and without S9 activation, on CH_2Cl_2 extracts. The small amount of sample obtained even in the tunnel precluded a full battery of tests. The tunnel membrane-filter samples consisted of one set collected over a series of diesel-dominated periods and another collected over a series of spark-ignition-dominated periods.

In the Aug/Sept experiment, strains TA98 and TA100 were used, with and without activation. The CH_2Cl_2 extracts and a few CH_3CN extracts were tested.

Results and Discussion

Total Particulate Mass Emission Rates. The gross particulate mass emission rates (mg/km) obtained for diesels and for spark-ignition vehicles are listed in Table II. These and values from earlier Turnpike tunnel experiments are listed also in ref 37. Results are expressed throughout as the mean ± standard deviation.

There was a continual tailwind in the tunnel, of average speed 26 km/h. This tailwind, together with the −0.5% roadway grade, should lower the fuel consumption rates (and hence presumably the particulate mass emission rates) of heavy-duty diesels by ~45% relative to no-wind level-road values (38). The heavy-duty diesel particulate emission rates in Table II are similar to values from dynamometer studies (41).

The difference in total mass per kilometer from diesels between May/June and Aug/Sept is statistically significant (109 ± 30 mg/km) and consists of a 20% increase in the unextractable material in Aug/Sept. This may be
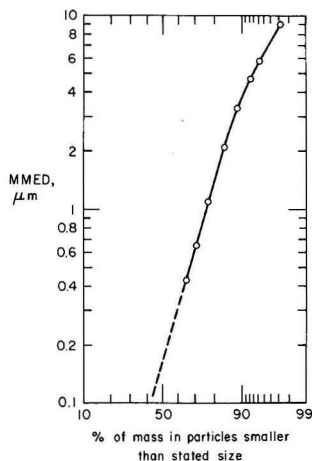
Figure 4. Particle size distribution for the vehicle aerosol, Allegheny Mountain Tunnel Aug/Sept 1979 experiment; log probability plot. Size distribution is for the sum of all impactor runs (72.5% spark-ignition vehicles).

related to the 8 °C difference in ambient temperature; diesel soot emissions are said (42) to increase substantially with increasing ambient temperature.

Organic-Extractable Mass Emission Rates. Table II shows the emission rates of material extracted in turn by CH_2Cl_2 (see also Figure 3), CH_3CN, and o-$Cl_2Ph + O_2$. The percent that each extract represents of the total particulate mass for each vehicle category is given in parentheses. For diesels the percentage extractable in CH_2Cl_2 is consistent with data from dynamometer studies (13, 17, 29, 30, 40) of light- and heavy-duty diesels.

Acetonitrile, a polar solvent, accounted for 6 ± 2% of the extractable diesel particulate matter at Allegheny and ~10% of the extractable material from vehicles as a whole. For comparison, in two diesel-particulate studies (11, 17) in which glass-fiber filter samples were extracted by CH_2Cl_2 followed by CH_3CN, 14–17% of the extracted mass was in the CH_3CN. In two other diesel-particulate studies (29, 43) where T60A20 or similar filter material was extracted by cyclohexane/CH_2Cl_2/CH_3CN in sequence, the average extract portion in the CH_3CN phase was ~20%.

Following the CH_2Cl_2 and CH_3CN extractions, extraction with o-Cl_2Ph in a stream of O_2 removed essentially no further material. Since Soxhlet extraction with o-Cl_2Ph + O_2 is effective for many organic compounds including polymeric material, this result implies that CH_2Cl_2 and CH_3CN had extracted nearly all of the organic material.

Particle Size Distribution. Figure 4 shows the particle size distribution from vehicles from the Aug/Sept experiment as a whole. This distribution can be considered to represent diesel particulate matter; even though diesels comprised on the average only 27.5% of the traffic during the impactor runs, they were responsible for better than 90% of the vehicle-associated particulate matter (see emission rates in Table II). In contrast to the intake-fan-room particulate matter, which had a mass median equivalent diameter (MMED) of 0.6 μm, the extrapolated MMED of the vehicle material was ~0.15 μm; 65% of the vehicle material was on the after filter, i.e., MMED <0.43 μm. As discussed in ref 37, these results agree entirely with published dynamometer/dilution-tube results on diesels.

HPLC Fluorescence Profiles. Figure 5 shows that the HPLC fluorescence profile of the tunnel-air particulate

Table III. Summary of HPLC Analyses by Ford Method No. 2, Allegheny Tunnel, Aug/Sept 1979

	ratio between diesel and spark-ignition fluorescence, counts/km[a]	distribution of fluorescence intensity by HPLC region, %			
		spark-ignition	diesels	all traffic	fan room[b]
CH₂Cl₂ extract					
PAH-1	34	4 ± 7	20 ± 2	15	9
PAH-2	15	6 ± 4	11 ± 1	9	3
PAH-3 + 4 + 5	3	51 ± 10	18 ± 2	29	40
ΣPAH	6	60 ± 18	50 ± 4	53	52
TRANS-1	9[c]	5 ± 1[c]	7 ± 0.3[c]	6[c]	4
TRANS-2	~1000[c]	0.007 ± 0.0004[c]	0.8 ± 0.1[c]	0.5[c]	0.03
TRANS-3 + 4	8	14 ± 6	14 ± 1	15	2
ΣTRANS	7	21 ± 8	21 ± 2	21	6
ΣOXY	9	20 ± 8	24 ± 2	22	37
CH₂Cl₂ total	7	99.7	95	96	95.5
CH₃CN extract (after CH₂Cl₂)					
ΣPAH	10[c]	0.5 ± 0.8[c]	0.7 ± 0.2[c]	0.6[c]	0.2[c]
ΣTRANS	∞[c]	−0.1 ± 1.2[c]	0.8 ± 0.3[c]	0.5[c]	0.09[c]
ΣOXY	∞[c]	−0.2 ± 1.5[c]	4 ± 0.4[c]	3[c]	4[c]
CH₃CN total	192[c]	0.2 ± 3.4[c]	5 ± 0.8[c]	4[c]	4.5[c]
grand total	7.4	≡100	≡100	≡100	≡100

[a] Average diesel-truck gross weight was approximately 30 tons. [b] The fan room air corresponds to local rural air slightly contaminated by Turnpike traffic emissions. [c] HiVol data only.
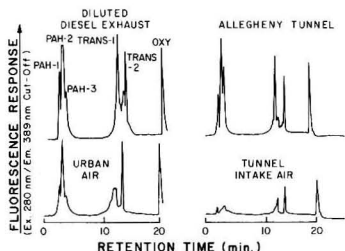
Figure 5. HPLC fluorescence profiles of CH₂Cl₂ extracts of airborne particulates collected from diesel exhaust diluted ~10:1 in a dilution tube, suburban air (Dearborn, MI), Allegheny Mountain Tunnel (May/June 1979, east portal left side, 142-mm Zefluor filter, traffic 87.8% spark-ignition), and simultaneously sampled east intake fan room air at Allegheny (142-mm Zefluor filter), by using the Ford method no. 1 elution (n-heptane/CHCl₃/CH₃CN) and normal-phase radial compression silica gel column. The OXY peak comes at 18–20 min depending on the timing of the CH₃CN injection.

extract closely resembles that of diesel exhaust particulate extract obtained in dynamometer/dilution-tube measurements.

Figure 5 suggests a tendency of polycyclic aromatic hydrocarbons (PAH's) toward higher molecular weights at Allegheny than in diesel exhaust in the dilution tube (compare peaks PAH-1 and PAH-3). This difference stems from the presence of spark-ignition vehicles at Allegheny and from the fact, documented in Figure 6 and Table III, that the PAH fluorescence intensity shifts to higher molecular weight PAH's as spark-ignition vehicles become more prevalent. (For definition of the chemical composition of the HPLC fractions, see Table III of ref 22. Generally, polarity and degree of oxidation increase from PAH to TRANS to OXY. In the PAH region of Figure 6, three- and four-ring PAH's generally elute in PAH-1, ≥six-ring PAH's in PAH-5, etc.) Results of regressions of peak areas per kilometer vs. traffic composition, summarized in Table III, lead to the following generalizations:

The fluorescence intensities of heavy-duty diesel emissions per kilometer are an order of magnitude greater than those of spark-ignition vehicles. On a
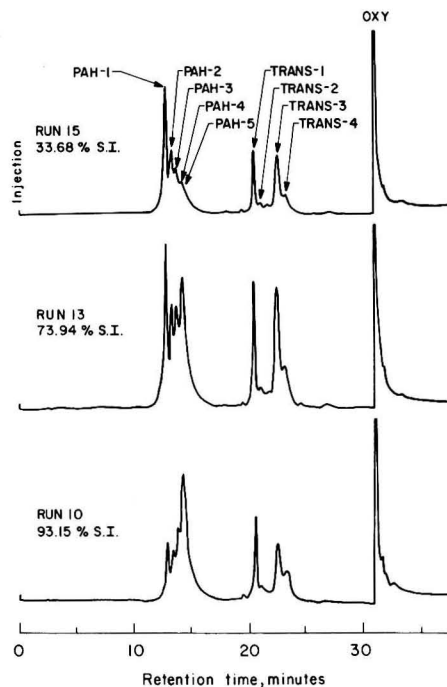
Figure 6. HPLC fluorescence profiles of CH₂Cl₂ extracts of Allegheny Mountain Tunnel samples (east portal left side, T60A20 HiVol filters, Aug/Sept 1979), using the Ford method no. 2 elution (n-hexane/CH₂Cl₂/CH₃CN) and normal-phase radial compression silica gel column. Traffic composition from visual counting is indicated for each trace (S.I. = spark-ignition vehicles).

fuel-specific basis, the ratio would be ~3.

In terms of fluorescence intensities, spark-ignition vehicles are deficient in low molecular weight PAH's relative to diesels. For example, the intensity ratio in Table III between diesel and spark-ignition-vehicle counts per kilometer is 34 for PAH-1 (the lightest

		TA98		TA100	
		−S9	+S9	−S9	+S9
142-mm Zefluor	run 8, 10, 12, east portal (91.6% spark ignition)	0.80	0.55[b]		
	intake fans[c]	1.04	0.11[b]		
	run 15, 17, 19, east portal (35.3% spark ignition)	0.56	0.35[b]		
	intake fans[c]	0.33	0.27[b]		
	long-term tower	0.19	0.08[b]		
T60A20 HiVol	run 7, 9, 11, east portal[d] (83.4% spark ignition)	0.82	0.71	0.67	0.99
	intake fans[c,d]	0.62	0.31	0.24	0.55
	run 8, 10, 12, east portal[d] (91.6% spark ignition)	0.45	0.42[b]		
	intake fans[c,d]	0.52	0.25[b]		
	run 13, 14, east portal[d] (77.3% spark ignition)	1.04	0.42	1.03	1.09
	intake fans[c,d]	0.76	0.66	0.53	0.76
	run 15, 17, 19, east portal[d] (35.3% spark ignition)	0.28	0.22[b]		
	intake fans[c,d]	0.46	0.44[b]		
	run 16, 18, east portal[d] (65.9% spark ignition)	0.82	0.49	0.75	0.75
	intake fans[c,d]	1.23	0.93	0.56	1.05
	long-term west intake, runs 7-19[c]	0.62	0.45[b]		

[a] Corrected for blank-filter CH₂Cl₂-extracted mass and mutagenicity. [b] Second determination (see text). First determination had invalid +S9 control and read 3.5 times higher on the average. [c] The fan room air corresponds to local rural air slightly contaminated by Turnpike traffic emissions. [d] Pooled HiVol samples.

PAH's) and only 3 for PAH-3 + PAH-4 + PAH-5.

In terms of fluorescence intensities, the vehicle-derived material differs from the fan-room material mainly in having more TRANS-3 and -4 and less OXY.

The CH₃CN extract represents only a small part of the total extractable fluorescence. Of the CH₃CN-extract fluorescence, the diesel is the principal source. The CH₃CN extract is far more extensively oxygenated than the CH₂Cl₂ extract, as expected.

The ratios in Table III between diesel and spark-ignition-vehicle fluorescence counts per kilometer are generally several times less than the mass emission-rate ratio of extractable material or of gross particulate matter (Table II). Thus:

Per unit mass of extractable or total particulate matter, material emitted by spark-ignition vehicles is several times more fluorescent than that emitted by diesels (not surprising, since most of the extractable diesel material is aliphatic hydrocarbons).

Figure 7 again documents the tendency for the diesel PAH fluorescence to be associated with lower molecular weights than the PAH fluorescence from spark-ignition vehicles. (See Table I for the translations between α, β, γ and PAH, TRANS, OXY.) Further, Figure 7 shows that the material collected in the fan rooms and especially at the tower is more oxygenated than the tunnel material, as might be expected. Formation of fluorescent artifacts by reactions involving the filter medium is not apparent, in that qualitative and quantitative comparisons by HPLC between the west intake fan room long-term T60A20 HiVol filter and the sum of short-term filters spanning the same period show good agreement ($\sim\pm8\%$ in the case of the planimetry data).

Molecular Weight Distributions. The GC molecular weight distribution of CH₂Cl₂-extracted diesel particulate matter at Allegheny is shown in Figure 8 for the Aug/Sept experiment; the May/June results are the same. The molecular-weight distribution for spark-ignition vehicles cannot be constructed accurately from the Allegheny experiments because there is too much diesel material.

Shown also in Figure 8 is the GC molecular weight distribution associated with a heavy-duty diesel in a dynamometer/dilution-tube experiment (40). It clearly resembles the distribution at Allegheny.
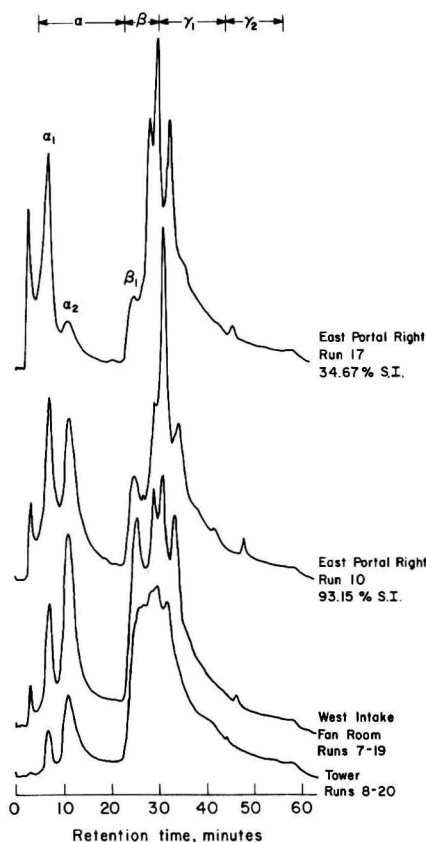
Figure 7. HPLC fluorescence profiles of CH₂Cl₂ extracts of Allegheny Mountain Tunnel samples (Aug/Sept 1979), using the EPA/RTP procedure. Traffic composition from visual counting is indicated for the two tunnel profiles (top to bottom): tunnel T60A20 HiVol filter with mostly diesel traffic; tunnel T60A20 HiVol filter with 93.15% spark-ignition-vehicle (=S.I.) traffic; west intake long-term T60A20 HiVol filter; tower long-term 142-mm Zefluor filter.

Mutagenicity. Table IV lists the Aug/Sept dose/response slopes expressed as revertants per microgram of

Table V. Mutagenicities,[a] Revertants per Cubic Meter of Air, Allegheny Tunnel, Aug/Sept 1979

		TA98		TA100	
		−S9	+S9	−S9	+S9
142-mm Zefluor	run 8, 10, 12, east portal (91.6% spark ignition)	22.6	15.3[b]		
	intake fans[c]	3.0	0.32[b]		
	run 15, 17, 19, east portal (35.3% spark ignition)	24.2	15.2[b]		
	intake fans[c]	1.4	1.1[b]		
	long-term tower	0.59	0.25[b]		
T60A20 HiVol	run 7, 9, 11, east portal[d] (83.4% spark ignition)	18.6	16.0	15.1	22.5
	intake fans[c,d]	2.1	1.0	0.79	1.8
	run 8, 10, 12, east portal[d] (91.6% spark ignition)	14.4	13.3[b]		
	intake fans[c,d]	1.8	0.8[b]		
	run 13, 14, east portal[d] (77.3% spark ignition)	47.8	19.4	47.4	50.2
	intake fans[c,d]	2.5	2.2	1.7	2.5
	run 15, 17, 19, east portal[d] (35.3% spark ignition)	13.6	10.8[b]		
	intake fans[c,d]	1.3	1.2[b]		
	run 16, 18, east portal[d] (65.9% spark ignition)	37.9	22.6	34.6	34.5
	intake fans[c,d]	3.4	2.6	1.6	2.9
	long-term west intake, runs 7–19[c]	1.8	1.3[b]		

[a] Corrected for blank-filter CH_2Cl_2-extracted mutagenicity. [b] Second determination (see text). [c] The fan room air corresponds to local rural air slightly contaminated by Turnpike traffic emissions. [d] Pooled HiVol samples.
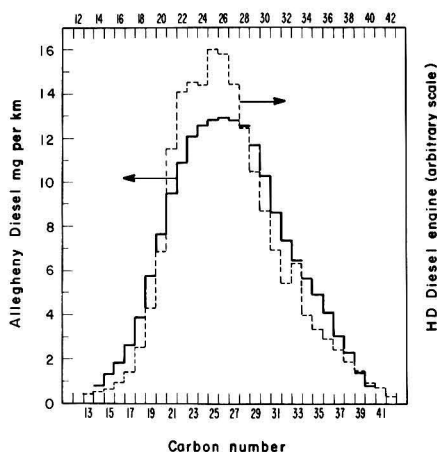
Figure 8. GC molecular weight distributions of CH_2Cl_2-extractable material: solid line and left ordinate, diesels in the Allegheny Mountain Tunnel Aug/Sept 1979 experiment; broken line and right ordinate, Caterpillar 3304 heavy-duty diesel engine at 2200 rpm (ref 40, Figure 12). The two plots are normalized to equal areas C_{14}–C_{40}. Arrows indicate the pairings of curves and ordinates.

Figure 9. Plot of Ames revertants/km vs. traffic composition, CH_2Cl_2 extracts, tester strain TA98 with microsomal activation (+S9), Allegheny Mountain Tunnel Aug/Sept 1979 experiment.

Table VI. Mutagenicities, Thousands of Revertants per Kilometer Traveled, CH_2Cl_2 Extracts, Allegheny Tunnel, 1979 (from Regression Analysis)

		spark-ignition	diesel trucks[a]
TA98 (−S9)	May/June	39 ± 24	211 ± 113
	Aug/Sept	19 ± 10	80 ± 20
TA98 (+S9)	May/June	26 ± 14	181 ± 40
	Aug/Sept	12 ± 4	51 ± 7
TA100 (−S9)	May/June[b]	5	221
	Aug/Sept	13 ± 32	135 ± 104
TA100 (+S9)	May/June[b]	22	271
	Aug/Sept	32 ± 27	88 ± 87
TA1535 (−S9)	May/June[c]	0	≤7
TA1535 (+S9)	May/June[c]	≤2.4	≤5
TA1537 (−S9)	May/June[b]	~2	<10
TA1537 (+S9)	May/June[b]	5	34
TA1538 (−S9)	May/June[b]	3	56
TA1538 (+S9)	May/June[b]	11	46

[a] Average gross weight approximately 30 tons. [b] Intake fan room values were not reasonable (too high) and are set to zero in calculating vehicle values for TA100, 1537, and 1538 in May/June. [c] Intake fan room samples were not tested on TA1535. Assumed zero.

CH_2Cl_2-extractable material, corrected for blank-filter CH_2Cl_2-extractable mass and mutagenicity. Even without further data reduction it is obvious that the mutagenicity, in revertants per microgram of CH_2Cl_2-extracted material, in the tunnel is similar in order of magnitude to that in the intake fan rooms or at the tower. Contamination by Turnpike traffic emissions accounts for most of the mutagenicity and CH_2Cl_2-extractable particulate mass in the fan rooms.

In Table V the Aug/Sept mutagenicities are expressed as revertants per cubic meter. The mutagenicity added to the tunnel air by vehicles is readily apparent; the mutagenicity per cubic meter in the tunnel air is an order of magnitude greater than in the intake air and some 50 times greater than in the air at the tower.

Regression of revertants per kilometer vs. traffic composition, as illustrated in Figure 9, gives the results listed in Table VI. The mutagenicity of heavy-duty diesel particulate emissions, expressed as revertants per kilometer, is seen to be much higher (median, ~6 times higher) than the revertants-per-kilometer mutagenicity of spark-ignition-vehicle particulate emissions.

The results in terms of revertants per microgram by vehicle category are summarized, together with revertants

Table VII. Mutagenicities, Revertants per Microgram of CH_2Cl_2-Extractable Material, Allegheny Tunnel, 1979

| | | vehicle type | | | | |
		spark-ignition	diesel	all	fan rooms[a]	tower
TA98 (−S9)	May/June	3 ± 2	1.1 ± 0.6	1.3	0.9[b]	c
	Aug/Sept	4 ± 3	0.4 ± 0.1	0.6	0.6	0.2
TA98 (+S9)	May/June	2 ± 1	0.9 ± 0.2	1.0	0.4[b]	c
	Aug/Sept	2.4 ± 1.6	0.27 ± 0.04	0.4	0.4 ± 0.15	0.08
TA100 (−S9)	May/June	0.4	1.2	1.0	d	c
	Aug/Sept	3 ± 7	0.7 ± 0.6	0.8	0.4	c
TA100 (+S9)	May/June	1.9	1.4	1.5	d	c
	Aug/Sept	7 ± 6	0.5 ± 0.5	0.9	0.7	c
TA1535 (−S9)	May/June	0	0.04	0.02	e	c
TA1535 (+S9)	May/June	0.2	0.02	0.06	e	c
TA1537 (−S9)	May/June	0.1	≤0.05	0.06	d	c
TA1537 (+S9)	May/June	0.4	0.2	0.2	d	c
TA1538 (−S9)	May/June	0.2	0.3	0.3	d	c
TA1538 (+S9)	May/June	0.9	0.2	0.4	d	c

[a] The fan room air corresponds to local rural air slightly contaminated by Turnpike traffic emissions. [b] 142-mm Zefluor samples only; fan-room T60A20 HiVol values were not reasonable (too high). [c] Not measured. [d] Intake fan room values were not reasonable (too high) and are set to zero in calculating vehicle values for May/June TA100, 1537, and 1538. [e] Not measured. Set to zero in calculating vehicle values.

Table VIII. Ratio of Normalized Mutagenicities[a] between CH_3CN and CH_2Cl_2 Extracts, Allegheny Tunnel, Aug/Sept 1979

	traffic (~64% diesels)	fan rooms[b]	tower
TA98 (−S9)	1.7 ± 1.5	~0.08	~3
TA98 (+S9)	0.18 ± 0.16	~0.004	0
TA100 (−S9)	0.53 ± 0.57	~0.02	0
TA100 (+S9)	~0.2	~0.03	

[a] Normalized Ames activity ≡ revertants per microgram of whole particulate matter (or per whole filter). A value of 1.7, for example, means that there was 1.7 times as much mutagenic activity in the CH_3CN extract of the whole sample as there was in the preceding CH_2Cl_2 extract of the whole sample. [b] The fan room air corresponds to local rural air slightly contaminated by Turnpike traffic emissions.

per microgram for traffic overall and for the fan-room and tower extracts, in Table VII. On a revertants per microgram basis the mutagenicity of the spark-ignition-vehicle particulate matter generally exceeds that of the diesel particulate matter (by a median margin of 2.5:1). The tower particulate material and the traffic material are similar, within an order of magnitude.

Table VIII indicates substantial mutagenicity in the CH_3CN extracts (i.e., mutagenicity not extracted by CH_2Cl_2) of the tunnel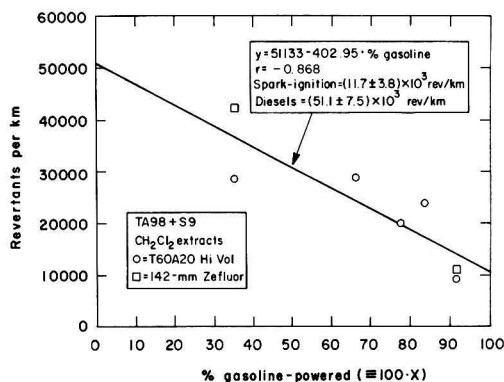 samples. The data are meager and the amounts of CH_3CN-extracted material are tiny so there is wide opportunity for error. In the only other study known to us that bears on this (11), CH_3CN is said to have extracted 30–50% as much TA98 activity (revertants per filter or per microgram of starting material) from diesel particulate matter as did a preceding CH_2Cl_2 extraction, consistent with our results and with the idea that much of the mutagenic material in diesel exhaust particulate matter is not extractable into CH_2Cl_2.

Uncertainties in the Mutagenicity Measurements. When half of the Aug/Sept TA98 (+S9) assays were repeated because of an invalid control, the new values were lower than the old by a factor of 3.5 on the average. The lower values were adopted in our work; the affected samples are identified in Tables IV and V. Use of the higher values would raise the mutagenicity estimates by a factor of 2.8 and would bring them within 20% of the May/June results given in Tables VI and VII. Also, the TA98 (−S9) assays of the Aug/Sept samples were tested in two sets,

and the disjunction between sets appears to be a factor of 2. The variation between the May/June and Aug/Sept experiments is a factor of 2 or 3—comparable to the uncertainties within experiments. A subsequent (1981) experiment at Allegheny (44) gave TA98 and TA100 (−S9) assays at Ford consistent with the 1979 results (generally closer to Aug/Sept).

By contrast, the standard deviation in measurement of other properties (e.g., total or CH_2Cl_2-extracted mass, Table II) is only a few percent. It follows that the scatter in the mutagenicity values has to do with the bioassay itself. This scatter, especially that from one time to another, seems consistent with month-to-month experience at EPA/RTP in other Ames assays during 1979–1980. At a given time the variation in Allegheny mutagenicity results is much greater than that seen at EPA/RTP with replicate dilution-tube samples; but in the Allegheny study the assay is being applied to a complex mixture that is possibly nonhomogeneous or unstable in dimethyl sulfoxide. Bacterial-population effects could cause 2- to 3-fold variations in dose/response slope (45). In the +S9 case, moreover, the variety of enzymes and their levels, the homogeneity of the mixture, the dissolved O_2 levels, etc., are essentially uncontrolled and incompletely characterized.

The pooled CH_2Cl_2 extracts of the fan-room T60A20 HiVol samples from the May/June experiment showed Ames activities in the range 3–20 (average, 7) revertants/μg, well above the values obtained via the concurrently collected 142-mm Zefluor filters and well above the Aug/Sept fan-room values (Table IV or VII); worse, the calculated revertants per cubic meter for the fan room (May/June T60A20 HiVol samples) would have exceeded the value for the tunnel. On these grounds, the May/June T60A20 fan-room data were rejected. The Zefluor data were used when available; otherwise the fan-room mutagenicity was set to zero in the calculations. The zero approximation should cause the mutagenicity of vehicle emissions in the tunnel to be overestimated, probably to an inconsequential degree.

There remains the question of sample age and long-term stability. The May/June samples were about 2 months old when tested by Ames assay. The Aug/Sept samples were 7 months old when tested. No trend with time was detected in five TA98 (+S9) assays and four TA98 (−S9) assays of one of the May/June east portal T60A20 samples over a span of 7.5 months, within the scatter of the mea-

surements (standard deviations ~55% of the mean). The half-order-of-magnitude agreement between May/June and Aug/Sept argues against drifts much larger than that, since the time lapses differed by 5 months. Some investigators report small changes on time scales of 2–5 months (13, 17). Claxton (28) reports no significant storage drift in dilution-tube samples over 7 months at 0 °C. It does not necessarily follow that the same would hold for samples with an ambient-aerosol component, but the storage temperatures for the Allegheny samples were much lower.

Comparison with Mutagenicity Results from Dynamometer/Dilution-Tube Studies. Comparison of dynamometer data in Tables IX and X with the Allegheny data in Tables VI and VII reveals no difference (within the broad range of the dynamometer data and the uncertainty in the Allegheny Ames-assay results) in mutagenicity of vehicle exhaust particulate emissions between on-road and dynamometer tests. Even the pattern of *relative* values among strains and between +S9 and –S9 at Allegheny is similar to the literature results.

The last statements take into account that the diesel results at Allegheny refer to heavy-duty diesels alone, and that the Allegheny diesel revertants-per-kilometer figures (though not necessarily the revertants-per-microgram figures) accordingly should be scaled down by a factor of 3 or so (38) in drawing comparisons with dilution-tube results for light-duty diesels. Moreover, heavy-duty diesels ordinarily have 2- and 4-stroke direct-injection engines, whereas diesel automobiles commonly have 4-stroke prechamber engines, and it appears from Tables IX and X that 2- and 4-stroke truck diesel engines do differ with respect to revertants per CH_2Cl_2-extracted micrograms or per kilometer.

Some 50% of the gasoline consumed in 1979 in the Allegheny Tunnel was consumed in catalyst-equipped vehicles (as judged by Turnpike service plaza figures (46) for the unleaded share of total gasoline sales). On a revertants-per-kilometer basis such vehicles contribute little to the mutagenicity associated with spark-ignition vehicle emissions (7, 19, 31) (see Table X). The emission rate (mg/km) of extractable organic particulate matter from catalyst-equipped vehicles is also very small (e.g., ref 47). Accordingly, the Allegheny spark-ignition revertants per microgram should be close to the revertants-per-microgram figure for noncatalyst systems, and the Allegheny revertants per kilometer should be intermediate between the revertants-per-kilometer figures for catalyst and noncatalyst systems.

There are two important qualifiers to the statement that mutagenicity and other properties are the same on-road and in dynamometer tests. First, the average age of the emissions at the point of measurement in the Allegheny Tunnel is only a few minutes, during which time the exhaust has been diluted by factors of ~10^3–10^4 (typical urban dilution factors are ~10^4) but there has been no exposure to sunlight; the Allegheny experiments do not address the difficult question of atmospheric effects over long transport times and distances. Second, a subsequent experiment at Allegheny (44) shows that 1-nitropyrene, usually a substantial contributor to the TA98 (–S9) mutagenicity of diesel exhaust particulate extracts in dilution-tube studies (48), is less than was predicted from such studies; the similarity between on-road and dilution-tube diesel properties evidently does not extend to chemical properties in detail.

Comparison with Mutagenicity Results of Other On-Road Studies. Results of other aerometric studies on vehicle exhaust mutagenicity are as yet sparse. Data from two highway tunnels in Japan (7) imply 0.29 ± 0.07 TA100 (+S9) revertants/µg of methanol-extracted material and lower values for TA98 (+S9), with indications that diesels are much more important in terms of revertants per distance traveled. Preliminary analysis of the EPA New York Port Authority Bus Terminal experiment (3) indicates general agreement with the Allegheny results.

As mentioned already, 1981 Allegheny mutagenicity results are comparable with those in the present work.

Comparison between On-Road and Ambient-Air Mutagenicities. Per microgram, the CH_2Cl_2-extractable particulate matter from diesels at Allegheny has about the same mutagenicity (Table VII) as is reported (49, 50) in organic extractable particulate matter in the Los Angeles Basin (e.g., 0.44 revertants/µg TA1538 (–S9), in Los Angeles). The same is true with respect to the Allegheny tower, within an order of magnitude (Table VII). At least in the case of the tower, however, the ambient material is chemically unlike the diesel material (e.g., see Figure 7), and thus the similarities in revertants per microgram may be fortuitous.

We can consider the introduction of light-duty diesels and the prospective changes in urban-air mutagenicity in light of the Allegheny results. Los Angeles is a good example because of the importance of vehicle emissions there. Let us imagine light-duty diesels of present design (particulate emission rate ~300 mg/km) supplanting 25% of the present-day automobiles. It can be projected (51) that under these circumstances light-duty diesels would add 8 µg/m^3 gross particulate matter or, if 24% extractable as at Allegheny (Table II), 2 µg/m^3 organic extractable material (vs. 15–35 µg/m^3 (52–56) now existing) to the Los Angeles atmosphere. If the emitted extractable material is mutagenically similar to that at Allegheny (~1 revertant/µg, Table VII), then 2 revertants/m^3 (TA98 (±S9) or TA100 (±S9)) would be added by light-duty diesels. (The *net* change, after subtraction of the mutagenicity associated with the supplanted spark-ignition vehicles as estimated from the Allegheny data, would be less.) This may be compared to Los Angeles values of ~100 revertants/m^3 recently reported (57) or ~2 revertants/m^3 as reported earlier (49, 50) by the same investigators.

It is useful to consider the eventual possibility of 25% light-duty diesels and 75% catalyst-equipped gasoline-powered automobiles in light of the situation that probably existed before the advent of catalyst-equipped automobiles in 1975. In Table X, automobiles operating on leaded gasoline and on diesel fuel seem similar with respect to revertants per kilometer. Aside from the effect of growth or decline in automobile usage, the eventual automobile-attributable atmospheric mutagenicity in a given place accordingly should be much the same as, or less than, whatever existed before 1975.

The foregoing projections deal only with the directly emitted particulate matter; photochemical aerosol and chemical changes in the atmosphere are ignored. It is stressed that the connection between Ames-assay mutagenicity and human carcinogenicity is an open question and that inferences about health effects lie beyond the scope of the present work. It would be especially unwarranted to speculate about relative health effects on the basis of relative mutagenicities of materials that are chemically very dissimilar (for example, diesel and Los Angeles organic particulate matter).

Relationships between Mutagenicity and HPLC Fluorescence Intensity. Correlations were sought between mutagenicities and HPLC fluorescence intensities. Samples from the tunnel, intake air, tower, and extract

Table IX. Summary of Ames Mutagenicities of CH_2Cl_2-Extractable Particulate Matter Generated in Dynamometer Experiments, Revertants per Microgram of CH_2Cl_2-Extracted Material

	TA98 −S9	TA98 +S9	TA100 −S9	TA100 +S9	TA1535 −S9	TA1535 +S9	TA1537 −S9	TA1537 +S9	TA1538 −S9	TA1538 +S9
noncatalyst spark-ignition systems, light duty										
5 1972 automobiles, leaded fuel (9)	0.7	0.8	0.85	0.9			0.13	0.2		
CFR engine, leaded fuel (9)	0.4	0.2	0.2	0.2			0.06	0.05		
4 in-use vehicles on HFET, leaded fuel (31)	8.5 ± 3.3	11 ± 3								
noncatalyst spark-ignition systems, medium duty										
1979 Ford V8-370 delivery truck, leaded fuel (31)		15								
1979 International Harvester V-345 delivery truck, leaded fuel (31)		17								
catalyst-equipped spark-ignition systems										
1977 Mustang (28)	1.4	3.4	2.0	2.3	0	0				
1978 Monarch on FTP (27)									5 ± 1	8 ± 7
16 in-use light-duty vehicles on HFET (31)	7 ± 8	7 ± 10							1.2 ± 0.2	2.0 ± 0.3
diesel systems, light-duty										
2 automobiles (17)	0.9	0	1.5	0.2	0.02	0.02	0.4	0.1	0.4	0.09
automobile (12)	1.4	0.32	3.1	1.0						
	1.8	1.4	4	1						
2 automobiles on various cycles (15, 16)	0.74									
European light-duty turbo engine (18)	7 ± 4	6 ± 6	6 ± 5	3.5 ± 4	0	0				
3 automobile engines (28)[b]	2.6 ± 1.7									
6 in-use automobiles on HFET and 50 mi/h cruise (13)[c]	1.2									
2 automobiles (14)	18.6									
Fiat 131 automobile on HFET (14)[d]	0.2 ± 0.01	0.7 ± 0.1 [e]	0.43 ± 0.06						0.17 ± 0.01	
3 automobiles on hot FTP (26)[e]	1.8 ± 0.4 [e]									
1980 Oldsmobile and 1980 Rabbit on HFET and 45 mi/h cruise (20)	2.6 ± 1.4									
2.3-L automobile on 1974 FTP hot (23)	0.54 ± 0.01	5.0 ± 0.4	1.12 ± 0.04							
5.7-L engine at 65 km/h road load (25)	5.9 ± 0.7									
2 automobiles (22)	12.5	0.8								
Nissan on FTP (27)	0.6									
Turbo Rabbit on FTP (27)										
1978 Oldsmobile 350 on FTP (27)										
diesel systems, medium- and heavy-duty										
Mercedes Benz 240D 4-cyl on HFET (5)	10.9	18.1	11.4	8.9			2.0	3.5	3.5	4.2
Mercedes Benz 240D 4-cyl on FTP (30)	3.2	0.9	3.9	1.9			0.2	0.3	2.9	2.5
2-stroke DDAD 6V-71 city bus engine (17)	0.09	0.13	0.4	0.3	0.02	0.01	0.02	0.02	2.5	1.9
2-stroke DDAD 8V-71 city bus engine (29, 31)		0.09							3.9	5.7
4-stroke Caterpillar 3108 medium engine (17)	2.6	1.7	4.4	4.0			0.5	0.3	0.7	0.8
4-stroke Caterpillar 3208 medium engine (21)[d]	0.5 ± 0.2	0.3 ± 0.2	0.7 ± 0.2	0.6 ± 0.3	0.01 ± 0.01	0.008 ± 0.006	0.10 ± 0.06	0.04 ± 0.03	0.4 ± 0.2	0.14 ± 0.17
4-stroke Caterpillar 3208 delivery truck (31)									0.07	0.12
4-stroke Caterpillar 3304 heavy engine (28)	0.66	1.1	1.7	1.15	0	0			1.3	1.7
4-stroke turbo Cummins J-6 (10)	~2	0.59								
4-stroke turbo Cummins JT-6-B1 (11)[f]	5.5	1.2								
4-stroke Cummins 290 (29, 31)		0.95								
4-stroke Mack ENDT 676 (29, 31)		1.2								

[a] Acetone extracts. Filters collected downstream of water-cooled condensers. [b] Revised from values given in ref 28 (Claxton, unpublished results, 1981). [c] Results at idle and on FTP and CFDS driving cycles are not included here. [d] Without a catalyst; measurements made with catalytic converters installed are not included here. [e] Benzene/ethanol (80:20 v/v) extracts. [f] CH_3CN extracts subsequent to the CH_2Cl_2 extraction showed TA98 (−S9) and (+S9) slopes of 1.7 and 0.5 revertants/μg, respectively.

Table X. Summary of Ames Mutagenicities of CH_2Cl_2-Extractable Particulate Matter Generated in Dynamometer Experiments, Thousands of Revertants per Kilometer Driven

	TA98		TA100		TA1535		TA1537		TA1538	
	−S9	+S9	−S9	+S9	−S9	+S9	−S9	+S9	−S9	+S9
noncatalyst spark-ignition systems, light-duty										
1976 Volvo 245L, leaded fuel (19)[a]	3 ± 2	5 ± 3								
4 in-use vehicles on HFET, leaded fuel (31)	101 ± 34	144 ± 100	6 ± 3	2.1 ± 0.1						
noncatalyst spark-ignition systems, medium-duty										
1979 Ford V8-370 delivery truck, leaded fuel (31)		375								
1979 Int. Harv. V-345 delivery truck, leaded fuel (31)		157								
catalyst-equipped spark-ignition systems										
1978 Monarch on FTP (27)	16 ± 16	16 ± 19								
16 in-use light-duty vehicles on HFET (31)									11 ± 7	19 ± 21
diesel systems, light-duty										
automobile (12)	84	0	150	21	2	2	35	10	41	9
1978 Peugeot 504 automobile (19)[a]	73 ± 10	(<73)	135 ± 6	(<135)						
6 in-use automobiles on HFET and 50 mi/h cruise (13)[b]	131 ± 51									
Fiat 131 automobile on HFET (14)[c]			94 ± 21							
1980 Oldsmobile and 1980 Rabbit on HFET and 45 mi/h cruise (20)	185 ± 143									
1978 Oldsmobile 350 on FTP (27)									247	187
Mercedes Benz 240D 4-cyl on FTP (30)	112	32	137	67	0	0	7	11	25	14
diesel systems, medium- and heavy-duty										
2-stroke DDAD 8V-71 city bus engine (29, 31)		30								
4-stroke Caterpillar 3208 delivery truck (31)		320								
4-stroke Cummins 290 (29, 31)		198								
4-stroke Mack ENDT 676 (29, 31)		146								

[a] Acetone extracts. Filters collected downstream of water-cooled condensers. Revertants/km values are derived from revertants/L of exhaust together with conversion factors given in ref 19. [b] Results at idle and on FTP and CFDS driving cycles are not included here. [c] Without a catalyst; measurements made with catalytic converters installed are not included here.

blanks were considered together. The test of generality of the relationship between mutagenicity and fluorescence intensity is therefore more severe than might be provided by diesel exhaust particulate samples alone.

Aside from data sets consisting entirely of intake-fan-room data, correlation coefficients are in the range 0.4–0.8. For comparison, atmospheric levels of species that are source-related generally have correlation coefficients ~0.8 (e.g., Pb vs. Br, $r = 0.983$) while atmospheric species un-related in origin have correlation coefficients ~0.4 because of meterological factors (58). From this perspective, it appears that HPLC fluorescence peak areas are not useful predictors of mutagenicity.

Conclusions

(1) The diesel particulate mass emission rate, particle size distribution, gross chemical properties (extractability into CH_2Cl_2, extract HPLC fluorescence profiles, and extract molecular weight distribution), and extract mutagenicity are essentially the same on-road at Allegheny as in dynamometer/dilution-tube experiments.

(2) Highway traffic produces a distinct increase in atmospheric near-road mutagenicity (revertants/m³, Table V).

(3) Per kilometer driven, the mutagenicities of the extractable particulate emissions from heavy-duty diesels are many times those from light-duty spark-ignition vehicles (about half of them equipped with catalytic converters).

(4) Per microgram extracted, the CH_2Cl_2-extracted particulate matter from diesels is less mutagenic than that from spark-ignition vehicles.

(5) Per microgram extracted, the CH_2Cl_2-extracted particulate matter from on-road diesels probably has mutagenicity comparable to ambient aerosol, both rural (only two measurements at the Allegheny tower) and as reported for the Los Angeles basin.

(6) The potential effect of light-duty diesels on urban atmospheric mutagenicity (revertants/m³) is equivocal, i.e., could be significant or insignificant depending on what is representative of current ambient levels.

(7) The mutagenicity of material extracted into CH_3CN following the usual CH_2Cl_2 extraction may be significant.

(8) HPLC fluorescence intensities probably are not useful predictors of mutagenicity.

(9) The fluorescing PAH's from diesels tend to be of lower molecular weight than those from spark-ignition vehicles.

(10) The main HPLC difference among vehicle particulate matter in the tunnel, in the intake fan rooms, and at the tower is that the latter two (especially the tower sample) are more oxidized, as judged by fluorescence intensities.

Implications of some of these conclusions are that (1) there would be some increase in near-road mutagenicity (revertants/m³ of air) if light-duty diesels were to supplant today's spark-ignition systems, but (2) the increase would probably not be disproportionate to the increment of CH_2Cl_2-extractable mass involved, and in any case (3) the dynamometer/dilution tube is probably a valid index of the on-road situation in a general sense (though this may not hold for detailed chemical composition).

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NOTES

Isolation, Identification, and Determination of Polycyclic Aromatic Hydrocarbons in Sewage

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■ A method for assaying 16 polycyclic aromatic hydrocarbons (PAH) is described. The analytical procedure for their isolation and quantitative determination with the use of an internal standard has been developed. High-pressure liquid chromatography with UV detection at 254 nm, on a Zorbax ODS column with methanol–water as the mobile phase, was applied for the determination of PAH in sewage samples.

Introduction

Polycyclic aromatic hydrocarbons (PAH) constitute a large group of compounds occurring in the atmosphere, soil, surface waters, sea water, and in many foodstuffs (1–5).

The most sensitive methods currently employed for assaying PAH are the following: (i) gas–liquid chromatography using isotropic capillary columns and nematic columns (6–10); (ii) UV spectrophotometry and spectrofluorimetry (11–13); (iii) high-pressure liquid chromatography (HPLC) (14, 15).

In this note we describe an analytical procedure we have developed for assaying PAH in sewage by using HPLC.

Experimental Section

Analysis of PAH requires extreme care at all stages in the analytical process. All solvents used were of high purity and glass distilled; the glass equipment must be throughly cleaned.

The samples were taken from the central stream of the sewage into 2 dm³ glass bottles.

Preparation of Florisil. A suspension of 300 g of Florisil in 500 cm³ of methanol was shaken for 1 min,

transferred onto a Buechner funnel, and allowed to drain into a suction flask. Florisil was washed on the filter twice with 150 cm³ of methanol, the residual being removed in vacuo. Finally, Florisil was dried for 3 h in a rotary evaporator under reduced pressure and kept in tightly closed vessels.

Before use, Florisil should be tested by using a standard benzo[a]pyrene solution and benzo[b]chrysene as internal standard. The recovery of the standard should be approximately 95%.

Determination: Isolation of PAH from Sewage. To a 2-dm³ sample of sewage was added 2 cm³ of a standard benzo[b]chrysene or picene solution (3.6 µg/cm³), followed by 200 cm³ of cyclohexane, and the mixture was mechanically stirred for 1 h. The cyclohexane fraction was separated, and the operation was repeated with another 200 cm³ of cyclohexane. The combined cyclohexane fractions were extracted with a 1-dm³ separating funnel three times for 2 min by using 100 cm³ of Me₂SO. After each extraction the lower layer (Me₂SO) was transferred to a 1-dm³ separating funnel containing 400 cm³ of distilled water. The cyclohexane phase was discarded, and the contents of the funnel were cooled to room temperature and extracted four times with 50 cm³ of cyclohexane. The combined extracts (200 cm³) were transferred to the 1-dm³ separating funnel containing 400 cm³ of distilled water. The cyclohexane layer was discarded, and the contents of the funnel were cooled to room temperature and extracted with four 50-cm³ portions of cyclohexane. The lower layer was discarded. The combined cyclohexane extracts (200 cm³) were placed in a 1-dm³ separating funnel and extracted with two 200-cm³ portions of a dimethylformamide (DMF)–water (9:1) mixture. The lower layers were placed successively in 2-dm³ separating funnels containing 400 cm³ of water, whereas the upper layers were discarded. The DMF–water layer (800 cm³) was extracted with two 150-

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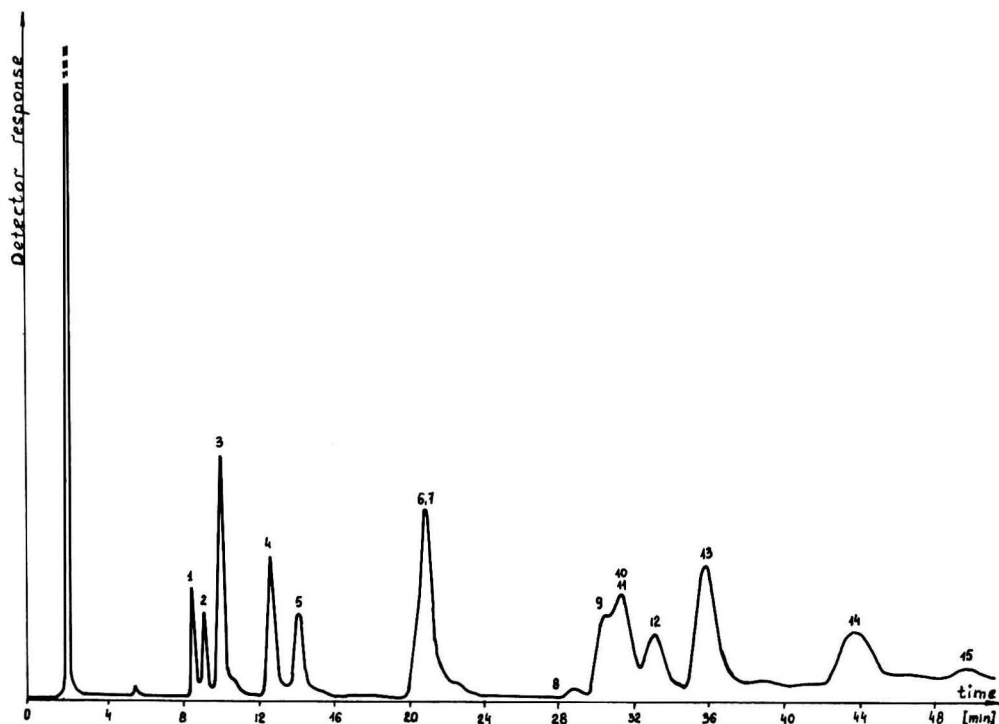
Figure 1. Separation of polycyclic aromatic hydrocarbons (PAH) standards: column, Zorbax ODS; mobile phase, methanol–water (80:20); flow rate, 0.8 cm³/min; column temperature, 30 °C.

cm³ portions of cyclohexane. The lower layer was discarded, and the combined cyclohexane extracts (300 cm³) were washed with distilled water to remove residual DMF. This cyclohexane extract was applied onto a chromatographic column packed first with 60 g of Florisil and then with 50 g of Na₂SO₄. The column was protected from light by being wrapped tightly with aluminum foil. Before use, the column was moistened with 100 cm³ of cyclohexane, the eluate being discarded. The eluate obtained after running through the column of 300 cm³ of the cyclohexane solution was likewise discarded. The adsorbed PAH fraction was eluted with 180 cm³ of benzene, the eluate being collected in a 250-cm³ round-bottomed flask. The benzene eluate was concentrated in a vacuum rotary evaporator to 3–5 cm³, transferred to a 10-cm³ conical test tube, and evaporated almost to dryness under nitrogen. The residue was dissolved in 100 μL of DMF and analyzed by HPLC.

The column (Du Pont Instruments, 4.6 × 250 mm) was packed with Zorbax ODS, grain size 5 μm, with the following conditions: column temperature, 30 °C; mobile phase, methanol–water (80:20 by volume); flow rate of the mobile phase, 0.8 cm³/min; chart speed, 0.5 cm/min.

Individual PAH were identified by comparison of their retention times with those of authentic specimens.

The content of particular components was calculated (in μg/kg) from the following equation:

$$X = ABC/DG$$

where A is the peak area of the compound to be assayed, B is the volume (cm³) of the internal standard added, C is the concentration of the internal standard (μg/cm³), D is the peak area of the internal standard, and G is the sample weight of sewage (kg). The surface areas of peaks

Table I. Values of Retention Times (t_r) and Correction Factors (S_K) of PAH

no.	compound	t_r, min	S_K
1	fluorene	4.10	6.4
2	phenanthrene	4.42	2.8
3	anthracene	4.85	0.61
4	fluoranthene	6.2	12.6
5	pyrene	6.4	19.8
6	benz[a]anthracene	9.2	8.0
7	chrysene	9.6	0.54
8	benzo[j]fluoranthene	13.2	64.6
9	benzo[e]pyrene	13.9	20.7
10	benzo[b]fluoranthene	14.4	6.6
11	perylene	14.4	5.6
12	benzo[k]fluoranthene	15.0	8.3
13	benzo[a]pyrene	16.2	6.4
14	dibenz[a,c]anthracene	18.3	8.3
15	dibenz[a,h]anthracene	21.4	29.5
16	benzo[b]chrysene	24.1	
17	benzo[ghi]perylene	24.5	15.9

A and B were calculated by multiplying the height of the peaks by their width at half-height.

Results

In Figure 1, the separation of the standard mixture of PAH is shown. The identities of the compounds corresponding to peaks 1–16 are given in Table I. Table I lists retention times (t_1) of particular PAH together with values of the correction factor (S_k) that accounts for molar absorptivities of the compounds.

The absorptivities were determined at 254 nm by using samples of standard substances and a Carl Zeiss spectrophotometer. The correction factor, S_k, of particular compounds indicates how many times the peak area must be
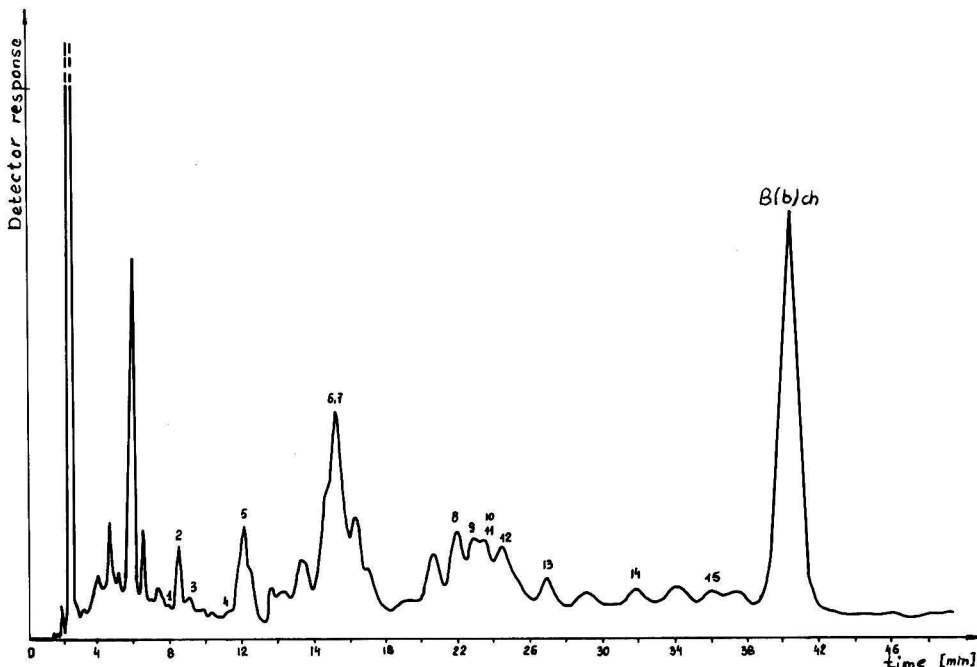
Figure 2. Separation of PAH fraction of sewage sample. Chromatographic conditions as in Figure 1.

multiplied to be able to compare it with the peak area of the internal standard, benzo[b]chrysene. In this way, differences due to various absorbance readings of the compounds at identical concentrations have been corrected. In figure 2 a chromatogram of the separation of the hydrocarbon fraction from a sewage sample is shown. In Table II the results of the determination of 16 PAH's in 16 sewage samples are summarized. The precision of the method was estimated as 3.6% in terms of standard deviation. The recovery was estimated by using doubly distilled water to which 15 identified PAH's were added at a level of 2 ppb each. The mean recovery was 90%.

Conclusions

The method enables simultaneous determination of 15 PAH's in sewage effluents. The use of the internal standard and correction factors, S_k, allows the elimination

of estimating the recovery after each run and the use of calibration curves for particular hydrocarbons. The method allows monitorization of the levels of PAH's, most of which are carcinogenic, in each discharge from the purification plant. This is particularly advantageous in industrial plants, for instance, operating oil refineries.

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A Deep-Towed Pumping System for Continuous Underway Sampling

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■ The system described here uses a hose–cable combination to tow a fishlike body containing a pump and a CSTD (conductive–salinity–temperature–depth) probe at depths of 135 m (or less) while the towing vessel is underway at speeds in excess of 5 m s^{-1} (10 kn). This survey unit has the capability of pumping 6 L/min of seawater to analytical equipment on deck while simultaneously measuring the salinity, temperature, and depth at which the towed body is deployed. An on-deck data acquisition system automatically records physical, chemical, and biological data and provides real-time displays that can be used to modify the design of the survey as it is conducted. Optimum utilization of this system requires a heavy investment in analytical equipment and is therefore best accomplished by multidisciplinary programs. Such operation generates far more data than are normally obtained by oceanographic vessels and can substantially increase the efficiency of research ship utilization for studies of the "mixed" layer.

Introduction

Studies of variability in the mixed layer of the ocean require sampling techniques that differ from the conventional oceanographic hydrographic cast taken on station. A variety of physical techniques have been developed for underway measurements by using in situ sensors with varying success, e.g., towed thermistor chains or expendable bathythermographs. Chemical studies generally are limited by the absence of effective in situ sensors; notable exceptions include the salinometer, oxygen electrode, and pH electrode. In situ fluorometers have also been deployed (*1*) for the estimation of chlorophyll, but most chemical measurements can only be done in the laboratory. For such measurements, detailed studies are best accomplished by pumping water continuously while underway from some selected depth or from various depths. The problems of doing so, various procedures attempted, and some of the successes are described in ref 2.

One system for underway sampling has been developed by the Department of Oceanography at Texas A&M University. The system described here has been modified from the original system described by Wiesenburg and Schink (*3*).

The System

Fish. The underwater vehicle ("fish") (Figure 1) is constructed from aluminum alloy and is controlled by lowering or raising the hose–cable. Our design relies, for the most part, on dynamic depression by the wing, which

gives it an effective weight of 225 kg at a speed of 5 m s^{-1}. The fish has good stability when towed through the water. It is convenient to handle and work on and is easy to launch and recover. Access is gained through a large hatch on top; space is available inside for additional sensors.

In Situ Instruments. Instruments mounted in the fish include a CSTD (conductivity–salinity–temperature–depth) unit and a pump–motor unit. The submersible pump, a 12-stage centrifugal (Berkeley Pump Co., Model 4AL12) is driven by a 1.5 HP submersible motor (Franklin Electric, Model 23431441) operating on 3-phase 220-V power. Seawater is pumped at the rate of 6 L min^{-1}. The pump delivers water at about 180 psi (1240 kPa) to the hose, which forms the core of the tow cable. An inlet pipe extends forward through the nose of the fish to sample water that has not come in contact with the body.

Cable and Fairing. The hose–cable (Consolidated Products) consists of 180 m of stainless steel armored jacket enclosing 20 electrical conductors (no. 20 copper wire) that are imbedded in plastic and are wrapped around a nylon hose. The two-layered armor braiding has a 4500-kg minimum breaking strength, far exceeding loads imposed by the fish. Power to, or signals from, the pump motor, CSTD, and other instruments mounted in the fish are provided through the conductors. The nylon hose (0.95 cm i.d.) transports water from the fish to the shipboard laboratory for analysis.

The cable is enclosed in a segmented fairing (Fathom Oceanology Flexnose fairing), which reduces the cable drag coefficient from 1.2 to 0.13, approximately doubling the depth achieved by the fish.

Winch and Framework. The winch and framework are shown in Figure 2. At its upper end the towing cable divides, with electrical connections passing through the drum axle to a slip-ring assembly and the cable hose connecting to a watertight rotary coupling on the drum hub. Only one layer of cable can be wound onto the winch drum because the rigid fairing stands straight out from the drum. The drum is 2.1 m in diameter and holds 27 turns of hose–cable plus fairing.

An articulated U-frame provides flexibility in handling the fish. The upper frame holds a 0.9 m diameter sheave on a screw-geared shaft, that serves as a level-wind for the cable. Hydraulic rams adjust the position of the upper frame and connect to a pneumatic accumulator, which serves as a shock absorber for transient stresses on the cable. The lower part of the frame can be pivoted out (hydraulically) to extend substantially beyond the stern of the towing vessel.

Other Shipboard Equipment. Analog signals from the CSTD are continuously recorded on a 12-pen strip chart recorder. The signals are also passed through an analog–digital converter and logged on a shipboard computer (Hewlett-Packard 2100A). During a recent cruise, water

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Ia

Ib

Ic
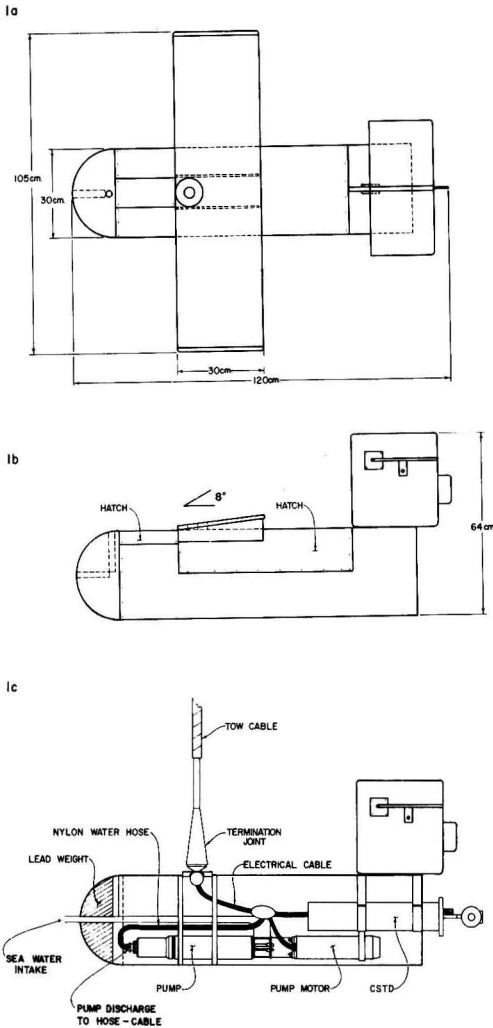
Figure 1. Towed pumping system underwater vehicle. The cable termination and some of the instrumentation mounted in the vehicle are shown in c. Weight of the fish with instrumentation in air is less than 100 kg.

from the submerged pump was supplied to a Turner Designs fluorometer fitted with a flow-through cuvette and to a 4-channel Technicon Autoanalyzer II system. Continuous fluorescence and nutrient measurements were logged on analog recorders and digitized by the computer system.

Data management is accomplished by using TALK, an interactive data acquisition and display program that stores data on disk and also transfers the data to magnetic tape for later analysis. The program logs time, windspeed, wind direction, and the ship's position. Chemical, physical, and biological data can be displayed and plotted as they are recorded. TALK also generates maps of the cruise track and several data reports.

Performance

The modified system was first deployed from the R/V GYRE on Cruise 80-G-6B in the Atlantic Ocean off the
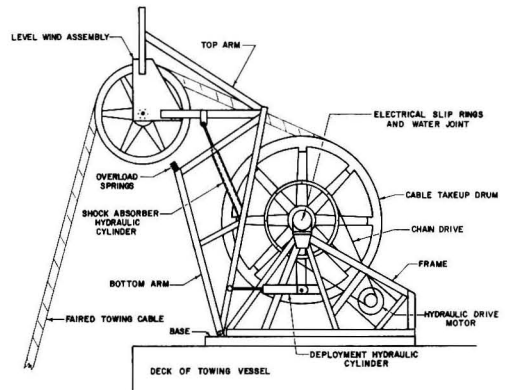
Figure 2. Towed pumping system winch, framework, and cable. System is ～5.5 m long, 3 m high, and 2 m wide and weighs ～2800 kg. System is bolted to deck of ship.
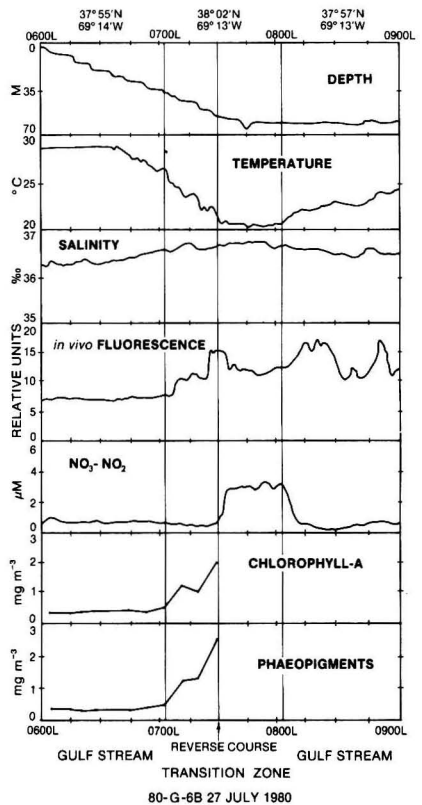
Figure 3. Continuous output of depth, temperature, salinity, in vivo fluorescence, and nitrate–nitrite from the deep-towed pumping system plus chlorophyll a and phaeopigment concentrations determined from water pumped to analytical equipment. Times and positions are noted.

eastern U.S. coast during July–August 1980, effectively collecting continuous underway measurements. Launching and recovery of the fish were easily and safely accomplished. When the arms of the framework are deployed outboard, the fish can enter or leave the water hanging from only 0.5 m of free cable. This virtually eliminates any swinging or banging of the fish against the stern of the

Table I. Properties of Turbulent Flow in a Hose

Constants for TAMU Towed Pumping System
u_0 = towing speed = 6 kn = 300 cm s^{-1}
L = length of hose = 200 m = 2 × 10^4 cm
a = inside radius 3/8 in. i.d. = 0.5 cm radius
Q = flow rate = 6 L min^{-1} = 100 cm^3 s^{-1}
R = Reynold's no.

Equations
u = mean flow velocity = $Q/\pi a^2$
  = $100(3.14 \times 0.5^2)^{-1}$ cm^3 s^{-1} cm^{-2}
  = 127 cm s^{-1}
R = Reynolds no. = $2au/\nu$ = 12 700
T = time delay through the hose = L/u
  = $2 \times 10^4(127)^{-1}$ cm cm^{-1} s
  = 157 s
S = sample smear^a = $(4.02 \times a \times L \times R^{-1/8})^{1/2}u_0u^{-1}$
  = $(4.02 \times 0.5 \times 20000 \times 0.307)^{1/2} \times 300 \times 127^{-1}$ (cm
    cm)$^{1/2}$ cm s^{-1} cm^{-1} s
  = 262 cm
T = smear duration = S/u_0
  = $262(300)^{-1}$ cm cm^{-1} s
  = 0.87 s

^{a} An impulse entering the hose exits approximately as a Gaussian distribution. Sample smear, S, is the standard deviation of that distribution. See Guinasso et al. (5) for the derivation of the sample smear equation.

ship during retrieval. The fish could actually be lanched or recovered single-handed, although normal practice involves two or three persons.

Deployment to maximum depth could be accomplished in 5 min, but recovery was slower because of the requirement that the fairing stand up perfectly straight as the hose is spooled onto the drum. When retrieving the fish the ship's speed was normally lowered to 4 kn (2 m s^{-1}), substantially reducing the strain on the hose–cable. However, both deployment and retrieval could be accomplished at full speed (5 m s^{-1}).

Some data obtained during R/V GYRE Cruise 80-G-6B suggest the potential of continuous deep-towed sampling. The fish was towed into a transition zone between the Gulf Stream and slope water at selected depths for various periods of time. The Oceanographic Analysis for this time period (4) shows the northern edge of the Gulf Stream bounded by a tongue of cool water extending from the east; to the north of this tongue there is a stream of warm water apparently flowing westward. This interweaving of water types results in a transition zone between Gulf Stream and slope water. We entered this transition zone at ~0700 as the ship steamed north. At 0730 the fish was lowered slightly and the ship turned around to steam south, leaving the transition zone and reentering the Gulf Stream proper at about 0800. Figure 3 shows a plot of depth, temperature, salinity, fluorescence, dissolved nitrate plus nitrite, chlorophyll and phaeopigments collected from 0600 to 0900. Corresponding changes can be observed in the various parameters as the fish is lowered and the Gulf Stream front is encountered. The chlorophyll a and phaeopigment concentrations were determined by standard laboratory analyses of water samples pumped from depth.

The deep-towed pumping system can explore chemical and biological properties that cannot be observed by in situ sensors, as the ship steams over different waters. Some smearing of the variations in water properties occurs as water passes up through the hose. Guinasso et al. (5) have

described problems inherent to pumping samples through long hoses: smearing and mixing in dead volumes. Table I gives characteristics of our system. One important conclusion is evident from their treatment: longer hose systems inherently degrade the resolution; and ship's speed must be reduced in proportion to hose length if resolution is to be maintained. Very high pressure pumps might partially overcome the loss in resolution due to hose length, but that remedy is limited.

Conclusions

Water samples and in situ measurements can be taken throughout the mixed layer while an oceanographic vessel is underway at speeds in excess of 5 m s^{-1}. This capability provides the potential for a great increase in our understanding of mixed-layer processes. Deployment of this system requires a heavy investment in associated analytical equipment plus an appropriate team of analysts and operators. A substantial program of data management must also be provided to utilize the full potential of this sampling system.

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Rates of Reaction of Hydroxyl Radicals with 2-(Dimethylamino)ethanol and 2-Amino-2-methyl-1-propanol in the Gas Phase at 300 ± 2 K

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■ The rates of the reactions of OH radicals with 2-(dimethylamino)ethanol and 2-amino-2-methyl-1-propanol have been determined by using a flash photolysis–resonance fluorescence technique to be $(4.7 \pm 1.2) \times 10^{-11}$ and $(2.8 \pm 0.5) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, respectively, at 300 ± 2 K. Implications of the increased use of these compounds (as paint solubilizers) on air quality are discussed.

The recent proposal by the California Air Resources Board (1) of a new policy to control solvent emissions from assembly line paint operations has led to the increased use of low-solvent (i.e., waterborne and high solids) coatings for these purposes. Such coatings contain (as solubilizers) significant quantities of amines, in particular 2-(dimethylamino)ethanol, $(CH_3)_2NCH_2CH_2OH$ (DMAE), and to a lesser extent, its structural isomer 2-amino-2-methyl-1-propanol, $(CH_3)_2C(NH_2)CH_2OH$ (AMP). The occurrence of such amines in these finishes raises the possibility that one air quality effect (i.e., reduction of oxidant formation) may be traded for another potential health effect (i.e., formation of nitrosamines or nitramines) from amine precursors and oxides of nitrogen in air (2, 3).

The major loss process for both DMAE and AMP in polluted urban atmospheres is expected to be reaction with the hydroxyl radical. Thus, we report here results of direct measurements of the absolute rate constants for the reaction of DMAE and AMP with hydroxyl radicals at 300 ± 2 K using the flash photolysis–resonance fluorescence technique.

The experimental technique employed involves formation of OH radicals in a flow system by pulsed vacuum ultraviolet photolysis of H_2O at $\lambda \geq 105$ nm and monitoring their resulting decay rates by detection of the OH resonance fluorescence band at 306.4 nm ($A^2\Sigma^+$, $\nu' = 0 \rightarrow X^2\Pi$, $\nu'' = 0$) with a cooled photomultiplier tube. This technique has been described in detail previously (5–7) and thus need not be discussed further here. The reaction was studied at 50 ± 1 torr total pressure of argon. The concentration of the amines in the argon flow was determined by UV absorption at λ 200–225 nm.

The observed decays of the hydroxyl radical concentration were always exponential, and the first-order decay rates are shown as a function of DMAE and AMP concentration in Figures 1 and 2, respectively. Variation of the flash energy by a factor of 2 had no effect on the decay rates within experimental error nor had an increase in the total pressure of argon to ~100 torr. The slopes of the least-squares lines shown in Figures 1 and 2 yield the following rate constants for the reaction of hydroxyl radicals with DMAE and AMP at 300 ± 2 K:

$$k_1(\text{DMAE}) = (4.7 \pm 1.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_1(\text{AMP}) = (2.8 \pm 0.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

The error limits reflect twice the standard deviation of the slopes in Figures 1 and 2 plus the estimated uncertainties (10%) involved in measuring flow rates, pressures, and optical density at the wavelengths used.

This is the first rate measurement for the reaction of OH with AMP to be reported in the literature, but Anderson

and Stephens (8) report a value of $(8^{+2}_{-1}) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} for OH + DMAE over the temperature range 269–364 K, which is about 40% higher than that obtained in this study. The reason for this difference is not clear, especially since the experimental method (8) was very similar to the present one (5–7).

Taking the average hydroxyl concentration in the urban atmosphere to be $\sim 3 \times 10^6$ molecules cm^{-3} leads to estimated lifetimes (l/e) for DMAE and AMP of approximately 2 and 4 h, respectively, under such conditions, for oxidation by OH radicals. It is interesting to speculate on the fate of the radicals produced in these reactions under atmospheric conditions. Although no mechanistic information was obtained in this study, comparison of the measured rate constants with those for OH reactions of other molecules containing similar groups can provide insight into the branching ratios for the possible mechanisms. Thus, consideration of the rate for OH + trimethylamine (6.2×10^{-11} cm^3 molecule^{-1} s^{-1} (9)) leads to the conclusion that H abstraction from each N-methyl group contributes $\sim 2.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} to the overall rate (or $\sim 0.67 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} per C–H bond). Further, the reactivity of the alcohols methanol, ethanol, and propanol toward OH (10, 11) may be used to deduce that the $-CH_2CH_2OH$ group contributes ~ 0.3–0.4×10^{-11} cm^3 molecule^{-1} s^{-1} to the reactivity of n-propanol. Hence, we may estimate the rate constant for OH + DMAE to be $\sim 6(0.67 \times 10^{-11}) + (0.4 \times 10^{-11}) \sim 4.4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, in reasonable agreement with the measured value. The slightly higher value of the measured rate constant may reflect higher reactivity for the N-bonded rather than C-bonded $-CH_2CH_2OH$ group. On the basis of this argument, we may conclude that H abstraction from the N-methyl groups dominates in the reaction of OH + DMAE and constitutes ~60–80% of the overall reaction. The subsequent reactions of the radical produced in this dominant path may be as follows:
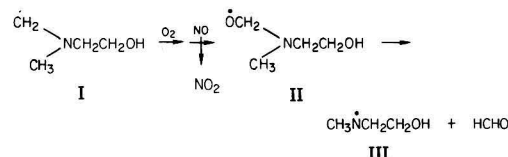
where scission of radical II is expected to occur more rapidly than H abstraction by O_2 from the radical center. The atmospheric chemistry of the dimethylamino (DMA) radical, which is analogous to the N-centered radical III, has been investigated by previous workers (2, 3, 12), who have concluded (12) that addition of NO and NO_2 to DMA to form nitrosamines and nitramines is in excess of 10^7 times faster than reaction with O_2. In sunlit atmospheres, which are a prerequisite for significant OH concentrations, the nitrosamine formed from III will rapidly photodissociate, thus it is likely that the major N-containing product from DMAE will be the photostable nitramine derivative of III, $CH_3(CH_2CH_2OH)NNO_2$.

Arguments based on the OH rate constants for methylamine (2.2×10^{-11} cm^3 molecule^{-1} s^{-1} (13)), ethylamine (2.8
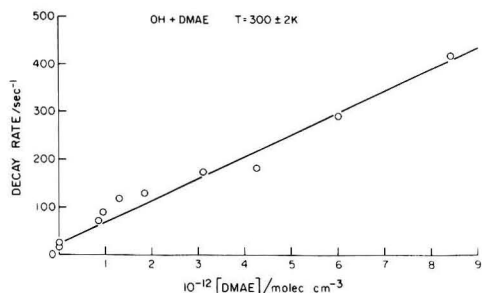
Figure 1. Pseudo-first-order decay rates of the hydroxyl radical concentration as a function of DMAE concentration at 300 ± 2 K.
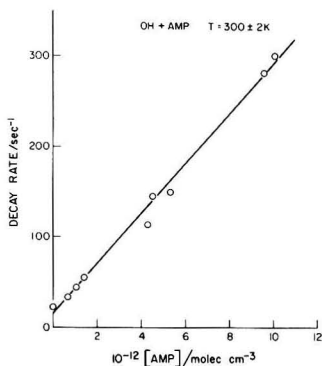
Figure 2. Pseudo-first-order decay rates of the hydroxyl radical concentration as a function of AMP concentrations at 300 ± 2 K.

$\times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (*11*)) and for ethanol (0.33×10^{-11} cm^3 molecule^{-1} s^{-1} (*10, 11*)) indicate that, although abstraction from C–H bonds usually is faster than from N–H bonds in primary amines, in the case of AMP the absence of hydrogen on the α carbon suggests that C–H abstraction would also be slow. Thus the reaction would most likely proceed by abstraction from the primary amino group giving radical IV.

$$
\begin{array}{c}
\text{CH}_3 \\
| \\
\text{CH}_3-\text{C}-\overset{\bullet}{\text{N}}\text{H} \\
| \\
\text{CH}_2\text{OH}
\end{array}
$$

IV
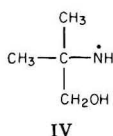
The only likely fates of radical IV under atmospheric conditions seem to be given in eq 1–3.

The suggested pathways involving loss of methyl (or methanolic) groups are somewhat unusual, and product studies of the photooxidation of AMP (or of the more symmetrical *tert*-butylamine) may prove instructive as well

$$\text{IV} \xrightarrow{+\text{NO}_2} (\text{CH}_3)_2(\text{CH}_2\text{OH})\text{C}-\text{N}\overset{\text{H}}{\underset{\text{NO}_2}{}} \qquad (1)$$

$$\text{IV} \xrightarrow{-\text{CH}_3} \overset{\text{CH}_3}{\underset{\text{CH}_2\text{OH}}{\text{C}}}=\text{N}-\text{H} \qquad (2)$$

$$\text{IV} \xrightarrow{-\text{CH}_2\text{OH}} \overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}=\text{N}-\text{H} \qquad (3)$$
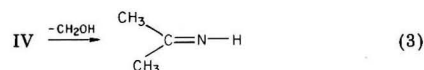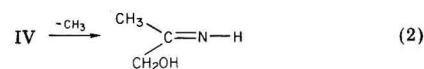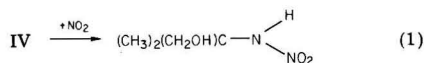
as aid in assessing the atmospheric yield of the nitramine from IV (analogues of which are carcinogenic in laboratory animals (*14, 15*)).

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Availability of Elements of Environmental Importance in Incinerated Sludge Ash

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■ An incinerated sludge ash from an industrialized urban area was analyzed by a sequential chemical extraction procedure to determine the chemical forms and potential availability of P, Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn. All 11 elements are relatively immobile with residual chemical forms comprising between 70% (P) and 97.7% (Pb) of the total elemental concentrations. The potentially toxic metals Cd, Cr, Cu, Ni, Pb, and Zn are ca. 90% in unavailable forms.

Introduction

Ever-increasing quantities of sewage sludge are inevitable byproducts of growing urban populations and industrial processes. An increasingly acceptable method of sludge management is incineration, which yields an ash weighing ca. 10% of the original dewatered sludge cake (*1–5*). Because the ash residue after incineration contains concentrations of metals ca. 4 times those found in dried sludge, with several at concentrations greater than 1% (*2, 3, 5, 6*), problems have been encountered in deciding upon final disposal sites because of concern about possible soil and groundwater contamination (*2, 3, 6*). Several options have been suggested for the ultimate disposal of the residue, e.g., in structural fill and road subbases, as a soil stabilizer, in concrete additive, and in building block material (*1*). Some measure of their mobility and bioavailability is required in order to evaluate the probable environmental effects of the high concentrations of potentially toxic metals and phosphorus in such residues. However, because of the complexity of biological systems there is no single bioassay technique that can be used to evaluate the availability of elements to terrestrial and aquatic plants and animals, including man, from soils, sediments and sludges (*5, 7, 8*). As a result there have been numerous studies that have employed a wide variety of chemical extraction procedures in order to assess the biological significance of elements in soils, sediments, and sludges. These procedures are usually based on the same principle—successive extractions of conceptually distinct lithological or authigenic fractions representing a scale of elemental forms ranging from the most mobile to those strongly bound to the support mineral. It would be unrealistic to expect a simple relationship between the concentrations of elemental forms in any one extract and their bioavailability. For example, for plants, elemental availability depends on prevailing soil conditions and on the element in question; elemental uptake is species dependent, and the concentrations will vary within the plant and as a function of the stage of growth (*7*). Nevertheless, chemical extraction procedures, though they may not be perfectly selective, can provide valuable information on the mobility and availability of elements in soils, sediments, and sludges to a variety of animals and plants (*7–13*).

In this note, we have determined the ease of leaching of P, Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn in in-

Table I. Analytical Conditions for D.C. Argon Plasma Atomic Emission Spectrometry

element	wavelength, nm	output slit[a]	limit of determination, mg L^{-1}
Al	308.22	A	0.050
Cd	228.80	A	0.008
Co	238.89	B	0.012
Cr	425.44	A	0.004
Cu	324.75	A	0.004
Fe	259.95	A	0.050
Mn	257.61	A	0.008
Ni	341.48	A	0.004
Pb	405.75	A	0.024
Zn	213.86	B	0.012
P	214.91	B	0.050

[a] Output slit dimensions: (A) 25 μm × 100 μm; (B) 50 μm × 200 μm. Input slit dimension: 50 μm × 200 μm.

cinerated sludge ash by using a sequential extraction scheme as described by Tessier et al. (*14*). This procedure was selected because it is one of the most thoroughly researched and analytically well-documented schemes available. The procedure will simulate to a certain extent the various environmental conditions to which this material may be subjected; deductions can thus be made about elemental levels that may be observed under these conditions in the environment.

Analytical Methodology

The sludge ash was obtained from the Hamilton (Ontario) Municipal Incinerator, which was operated at temperatures ranging from 760 to 960 °C. The secondary digested sludge was filtered on Komline–Sanderson coil vacuum filters prior to being fed to the multiple-hearth (9) BSP incinerator. The ash was ground to pass a 200 mesh screen and mixed by rolling for 24 h to ensure homogeneity. Six 2.0-g subsamples were weighed into 50-mL polysulfone (DuPont) centrifuge tubes. The extraction procedure partitions the elements into the following five fractions (*14*):

Fraction A. Exchangeable Metal Ions. The ash samples were extracted for 10 min with 8 mL of 1 M MgCl$_2$ at pH 7.0, with continuous agitation using a Burrell wrist-arm shaker.

Fraction B. Surface Oxide and Carbonate-Bound Metal Ions. The residue from A was extracted for 5 h with 8 mL of 1 M sodium acetate adjusted to pH 5.0 with acetic acid. Continuous agitation was maintained during the extraction.

Fraction C. Metal Ions Bound to Fe–Mn Oxides. The residue from B was extracted for 6 h at 90 ± 5 °C with 20 mL of 0.04 M hydroxylamine hydrochloride in 25% (v/v) acetic acid, with occasional agitation.

Fraction D. Metal Ions Bound to Organic Matter and Sulfides. The residue from C was extracted with 3 mL of 0.02 M nitric acid and 5 mL of 30% hydrogen peroxide (adjusted to pH 2) by slowly heating the mixture in a water bath to 90 ± 5 °C. The samples were periodically agitated, and after 2 h a second 3-mL aliquot of 30% hydrogen peroxide was added and the mixture heated to

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Table II. Distribution of the Chemical Forms of 11 Elements in Hamilton Incinerated Sludge Ash ($n = 6$; Units in $\mu g \ g^{-1}$ or % (Dry Weight))

fraction		Al	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn	P
A	mean	nd	nd	nd	1.9	nd	nd	0.08	0.08	nd	nd	3.4
	SD[a]							0.03	0.01			0.9
B	mean	0.6	nd	nd	0.1	nd	nd	5.1	0.7	2	nd	13
	SD	0.1			0.04			2.2	0.3	0.2		7
C	mean	30	0.11	2.7	4.1	1.1	110	118	13.5	25	480	1120
	SD	7	0.05	0.6	0.5	0.4	20	36	1.0	3	50	230
D	mean	1180	1.1	5.3	10.0	300	21.0	240	22	28	850	11 770
	SD	340	0.2	0.9	2.6	50	70	50	3	8	140	2 670
E	mean	4.25%	9.7	130	5260	2560	13.4%	1400	726	2220	12 080	30 900
	SD	0.20%	1	7	200	110	1.2%	100	40	100	380	2 700

[a] Standard deviation. [b] None detected.

90 °C as before. After 3 h, 5 mL of 1.2 M ammonium acetate in 10% (v/v) nitric acid were added, and the samples were diluted to ca. 15 mL and agitated for 30 min.

Fraction E. Residual Metal Ions. The residue from D was dislodged and transferred to a Teflon beaker with a fine spray of 0.02 M nitric acid. The slurry was simmered overnight with the addition of 10 mL of aqua regia and 3 mL of 30% hydrogen peroxide. The volume was carefully reduced to ca. 2 mL, and 10 mL of hydrofluoric acid and 3 mL of 30% hydrogen peroxide were added. Finally, 5 mL of concentrated hydrochloric acid and 10 mL of distilled water were added, and the solution was heated for $^1/_2$ h. The final extract was made up to 100 mL in a volumetric flask and stored in a polyethylene bottle.

The extractions, A–D, were carried out in 50-mL centrifuge tubes; after each extraction separation was effected by centrifuging (Sorvall SS-3) at 13 000 rpm (20 000g) for 30 min. The supernatants were decanted and made up to 25 mL (fractions A and B) or 50 mL (fractions C and D) and stored in polyethylene bottles. All samples were kept at 4 °C until they were analyzed. The concentrations of the 11 elements were determined by D. C. Argon Plasma Atomic Emission Spectrometry (DCPAES) by using a Spectraspan III three-electrode system (Spectrametrics Inc.) equipped with a multielement cassette and a DBC-33 background compensator module. The analytical conditions are summarized in Table I. All determinations were made by using the Hi 12 position on the DBC-33 background compensator. The Cd determination was done separately by using the 228.80-nm line in conjunction with the background compensator set at the Hi 12 position. It was found that for these extracts insufficient compensation was obtained by using the multielement cassette in which the line selected for Cd is 214.44 nm. Prior to running samples, the DBC-33 was used to obtain emission spectra of pure single-element standard solutions (2 mg L^{-1} concentrations) and the various sample matrices; on the basis of these spectra, which span ca. 1 Å on each side of the emission peak wavelength, the Hi 12 absolute correction option was selected as a compromise for the 11 elements. In the case of Cu, Ni, Zn, and P, correction had little or no effect on the analytical results. The need for background compensation was found to be necessary in most cases for Cd, Co, Cr, and Pb. Calibration stability was monitored every seventh sample (matrix change). Recalibration was done when the standard run as a sample showed a 10% drift.

Results and Discussion

The distribution of the 11 elements in the five fractions are presented in Table II. For each element, the sum of the five fractions has been compared (Table III) with the recommended total metal concentration data reported by

Table III. Comparison of Total Elemental Concentrations in Hamilton Incinerated Sludge Ash (Units in $\mu g \ g^{-1}$ or % (Dry Weight))

element	this work	ref 15	ref 16
Al	4.36 ± 0.20%	3.8 ± 0.6%	
Cd	10.9 ± 0.9	9 ± 1	
Co	140 ± 7		100
Cr	5280 ± 200	5200 ± 600	4870
Cu	2870 ± 110	2500 ± 300	
Fe	13.5 ± 1.1%	13.0 ± 1.0%	14.6%
Mn	1750 ± 100	1500 ± 100	
Ni	760 ± 45	640 ± 100	690
Pb	2270 ± 100	1600 ± 400	
Zn	13 440 ± 1100	14 000 ± 3000	13 900
P	43 810 ± 1150	50 000 ± 4000	

Knechtel and Fraser (15) and the neutron activation analyses communicated by Van der Sloot (16) for subsamples of the same incinerated sludge ash analyzed in this study. The precision of the total element concentrations for the present work is in all cases better than 10% and for seven elements less than 5%. There is acceptable to good agreement with the other reported data except for Co and Pb. The spectra for Pb indicate that the peak emission is superimposed on a high sloping background; the 238.89-nm Co line also shows elevated background intensities. The results in Table III indicate that background compensation is not completely effective for these two elements.

From an environmental impact perspective, the data in Table II show that in general, the 11 elements are relatively immobile with the residual forms accounting for at least 70% (P) to 97.7% (Pb) of the total elemental concentration. The potentially toxic elements, Cd, Cr, Cu, Ni, Pb, and Zn are 90% in unavailable forms.

The small but measurable amounts of Al, Cr, Mn, Ni, Pb, and P present in fractions A and/or B could be released if the sludge ash were to come in contact with ice and snow-melt contaminated with road salt or as a result of contact with acid-laden snow-melt or acidic rainfall (17). The elemental forms in fraction C are potentially mobile under reducing conditions. However, migration of these forms would be limited by precipitation occurring as oxidizing horizons and/or mixing with oxygenated water. Because sulfides and organic matter are decomposed during incineration, the elemental concentrations measured in fraction D likely indicate attack of the refractory residual phases which are nonavailable.

The preceding results can be contrasted with those of Stover et al. (18), who reported that Cd and Pb in sludge were mainly associated with carbonates, whereas Cu and Ni were found mainly as sulfides and exchangeable forms, respectively, and only ca. 10% of these two metals were in an organic form. Zn was present mostly in an organic

form (56%). In a study of a soil amended with sludge highly contaminated with Zn, Ni, Cu, and Cr, these elements were found to persist for 10 years in readily extractable forms that were available to grasses and clover (13).

Thus, although Hamilton incinerated sludge ash contains highly elevated phosphorus and trace-metal levels, their ease of leaching is quite small, and hence they would not be expected to pose a high degree of hazard to biological systems. Because Hamilton is the location of the largest steel works in Canada, the results of this study are perhaps more relevant to cities in which the iron and steel industry is important, e.g., Pittsburg and Sheffield.

Registry No. P, 7723-14-0; Al, 7429-90-5; Cd, 7440-43-9; Co, 7440-48-4; Cr, 7440-47-3; Cu, 7440-50-8; Fe, 7439-89-6; Mn, 7439-96-5; Ni, 7440-02-0; Pb, 7439-92-1; Zn, 7440-66-6.

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CORRESPONDENCE

Comment on "Effect of Nitrogen Oxide Emissions on Ozone Levels in Metropolitan Regions", "Effect of NO$_x$ Emission Rates on Smog Formation in the California South Coast Air Basin", and "Effect of Hydrocarbon and NO$_x$ on Photochemical Smog Formation under Simulated Transport Conditions"[†]

SIR: During the current review of the Clean Air Act and state and local reassessments of emission control strategies for meeting air quality standards (AQS), the issue of the relative effectiveness of strict control of oxides of nitrogen (NO$_x$) vs. reactive hydrocarbons (HC) in reducing ambient levels of ozone has again emerged as a critical area of debate.

For example, scientists at the General Motors Research Laboratories have recently argued in effect (1, 2) that proposed strategies involving more stringent control of NO$_x$ will be counterproductive in reducing ambient ozone in California's heavily impacted Los Angeles (LA) air basin.

Additionally, Innes (3) recently stated "The current strategy of reducing both HC and NO$_x$ emissions appears

to have been ineffective." He concluded, partly on the basis of his analyses of certain of our earliest smog chamber data (ca. 1974–1975) (4), that for the Los Angeles basin "This suggests that the ozone standard could be met throughout the basin with a reasonable increase in NO$_x$ emissions together with a similar decrease in HC emissions."

We have read these papers with interest and, because of our deep concern over the possible consequences to our nation's health and environment if such a strategy change were implemented, we feel compelled to reply. We shall address here all three of these papers since they deal with the same major issues concerning current oxidant control strategies of the U.S. Environmental Protection Agency (EPA) and the California Air Resources Board (CARB).

The evidence cited by these authors in support of their position does not lead us to revise our long-held view (5) that while strict controls of both HC and NO$_x$ may be more expensive, the greatly increased benefits to public health and the environment far outweigh the additional costs. In fact, there are several major problems with these papers:

(a) Glasson (1) and Innes (3) use data from experiments carried out in smog chambers under highly restricted and artificial conditions (e.g., irradiations at constant light intensity of 6–22 h duration) and readily extrapolate them to the ambient atmosphere. Chock et al. (2) similarly extrapolate their trajectory model simulations of several hypothetical air parcels in California's South Coast Air Basin (CSCAB).

[†] References 3, 2, and 1, respectively.

As atmospheric chemists with some experience in the design, construction, and operation of a variety of environmental chambers (4, 6) and computer modeling of chamber data (7, 8), we have learned that extrapolation of results from any environmental chamber experiment to ambient atmospheric conditions must be carried out with extreme caution. Thus, while the great majority of smog chamber experiments (Glasson's included) involve continuous irradiations simulating single-day conditions, severe air pollution periods in the CSCAB typically consist of multiday episodes that involve a high degree of day-to-day carryover (9) of such key pollutants as NO_2, peroxyacetyl nitrate (PAN), formaldehyde (HCHO) and higher aldehydes, and nitrous acid (HONO).

The noncriteria pollutants formaldehyde, nitrous acid, and PAN are the major early morning sources of hydroxyl radicals (OH), which drive the oxidation processes involved in photochemical smog (10, 11); as such their concentrations are critical inputs to any simulation model. Unfortunately, until recently there has been little information available on the actual ambient levels of these noncriteria pollutants as a function of altitude, time of day, and location in the CSCAB. For example, ambient nitrous acid data were nonexistent until our recent long-path-length spectroscopic studies showed significant levels (up to 8 ppb) during night and early morning hours at downtown Los Angeles (DTLA) (12) and somewhat lower levels at several downwind locations (13).

Furthermore, neither the data from single-day chamber irradiations nor time–concentration profiles developed from 10–12-h computer simulations can adequately describe Southern California's complex nighttime smog chemistry and meteorology. In particular, the stable meteorological conditions that generally occur at night result in a significant stratification of pollutants that cannot be simulated in smog chambers or by models validated against smog chamber data.

Finally, another problem with extrapolating smog chamber data to the ambient atmosphere arises from the occurrence of chamber-specific heterogeneous processes. The major chamber effects relevant to NO_x control are heterogeneous N_2O_5 hydrolysis (7) and chamber-dependent excess radical sources (7, 14, 15). Thus, we have recently demonstrated that unknown sources of OH radicals are important in smog chamber systems (14, 15), and this effect must be taken into account when applying chamber results to the atmosphere. Indeed, our calculations have shown that the presence of radical sources significantly alter the predicted effects of NO_x on O_3 formation (16).

(b) The papers by Chock et al. (2) and Innes (3) have some significant scientific problems; the latter paper also contains serious errors and, we feel, omissions of relevant information. We shall treat these later.

(c) These authors either ignore (1, 2) or oversimplify and confuse (3) certain critical air quality issues such as (i) the relative health impacts of O_3 vs. NO_2 and its associated nitrogenous copollutants and (ii) the potential impact of increases in NO_x emissions on ambient levels of nitric acid and nitrate aerosols. Such problems face not only southern Californians but residents of air basins throughout the U.S. impacted by photochemical smog and/or acid rain.

For example, although NO_2 time–concentration profiles were determined by Glasson (and maximum NO_2 values were shown to increase with increasing initial NO_x concentrations), no experimental data were reported for the species PAN and HNO_3 (1). These are formed along with O_3 and NO_2 (in chambers and ambient atmospheres) and determinations of their yields as functions of initial NO_x levels are required for an understanding of reaction

mechanisms in irradiated $HC–NO_x$–air systems, as well as for assessing air pollution impacts on health, agriculture, and the environment associated with increasing NO_x emissions.

In this regard, Spicer (17), in his very recent study, "Nitrate/Precursor Relationships in Urban Air—A Smog Chamber Investigation", obtained good nitrogen balances (>90%) in his irradiated $HC–NO_x$ systems and made accurate measurements of nitric acid and PAN concurrently with O_3 and NO_2. He observed that for a given HC mix there was a linear relationship between $[HNO_3]_{max}$ and initial NO_x concentrations and concluded "At HC/NO_x ratios typical of morning conditions in many cities, i.e., ~5–10, 25–50% of the initial NO_x can be converted to organic and inorganic nitrate within the first three hours of reaction."

He further showed that initial NO_x is transformed almost totally into PAN and HNO_3. Since PAN is thermally unstable (18), it is degraded to NO_2 and hence to HNO_3. Thus, the ultimate atmospheric sinks of NO_x are mainly HNO_3 (or nitrate particulate), together with much lesser amounts of organic nitrates. These results (17) are highly relevant to the NO_x vs. HC controversy because they experimentally confirm the view that increasing NO_x emissions will ultimately lead to a proportionate increase in nitrate levels (as nitric acid or particulate nitrate), which will be manifested as acid rain, acid fog, or dry deposition.

In summary, increasing NO_x emissions will lead to increased frequency and severity of acid fogs (19) as well as of acid rain. This is not only of concern in California (20) and other western states, but also in the northeastern United States and Canada, as well as in northern European countries.

Now let us consider in somewhat more detail the paper by Chock et al. (2). Our major concern is that these authors drew such generalized conclusions about the atmospheric consequences of relaxing NO_x control strategies in southern California on the basis of several 1-day simulations using a trajectory model of limited reliability and/or applicability to the CSCAB. For example, as stated earlier, 1-day computer simulations cannot reliably predict ozone and NO_2 levels during typical multiday smog episodes. Indeed the authors tacitly acknowledge this in their statement "Since the model does not take into account vertical wind and vertical wind shear, its application should be confined to a daytime, nonstagnant, convective period over relatively smooth terrain."

Furthermore, the chemical model they employed (21) must now be regarded as being outdated and deficient in several respects. While the effects of such deficiencies in the chemical mechanism on computer time–concentration profiles cannot be predicted a priori, clearly newer, and more chemically accurate, mechanisms should be employed. Furthermore, the ability to simulate the multiday episodes associated with the highest pollutant levels must be developed before substantial faith can be placed in the predictions of such simulations.

Although Chock et al. (2) state "However, like the grid models, because of the lack of measurements for most chemical species, estimations are required in specifying the initial conditions", they do not emphasize that the results obtained with their model are critically dependent upon the particular initial conditions chosen (21, 22). This could be especially important since their two trajectories start at 0700 near DTLA, which, at that time of the morning, usually has an atmosphere already heavily polluted with ozone precursors (both fresh emissions and any pollutant carryover from previous days), many of whose concentrations are unknown.

There are also significant discrepancies between the model "base-case" predictions and the actual air quality data against which the model was tested. For example, on Oct 15, 1973 (a moderate O_3 day), the measured $[NO_2]_{max}$ was 0.32 ppm (at 1100), but the base-case prediction was only ~0.16 ppm, a discrepancy of a factor of 2. In addition, for the base run of July 31, 1973 (a high ozone day), the authors state "the agreement is good for NO and NO_2 and acceptable for O_3 and CO." In fact there is again a difference of a factor of 2 between the measured NO concentration (0.08 ppm) and that calculated by the model (0.04 ppm) at 0800.

Additionally, we do not find "acceptable" a difference of more than a factor of 2 between the observed $[CO]_{max}$ of 6 ppm at 1300 and a calculated value at that time of only 2.5 ppm. Also troublesome is the fact that the calculated $[CO]_{max}$ occurred 5 h earlier at 0800. The fact that their model predictions (or its input) are this inaccurate for carbon monoxide, an essentially "nonreactive" primary pollutant, indicates a serious problem with their emissions and/or transport submodels. Given their difficulty with a nonreactive tracer species, we fail to see how one can have a great deal of confidence in their model predictions for the secondary pollutants ozone, PAN, and nitric acid, where complex chemistry must also be taken into account.

We do not cite these discrepancies to demean the role of modeling in atmospheric chemistry, nor do we fail to realize that air pollution models may be more useful in predicting relative rather than absolute changes in pollutant levels as emissions are altered. However, it is important that the nonexpert reading their paper be given some perspective on the state of the art of airshed modeling and the question of what constitutes "good" or "acceptable agreements".

Turning now to the paper by Innes (3), in his first paragraph he states "Maximum ozone concentrations in the Los Angeles basin, instead of decreasing with the advent of catalytic converters, have increased from ca. 0.35 to 0.45 ppm from 1975 to 1979." Apparently on this basis he then concludes "The current strategy of reducing both HC and NO_x emissions appears to have been ineffective." and strongly implies that various modeling studies show that only the imposition of NO_x controls offers a satisfactory explanation for the purported increase in O_3 maxima in Los Angeles from 1975 to 1979.

We are surprised to see that Innes drew such broad conclusions based on only these two data points. It is well recognized that in the CSCAB such relatively short-term air quality trends reflect primarily the effects of year-to-year differences in meteorology rather than significant changes in the emission inventories of HC and NO_x. In fact, total emissions of NO_x were virtually unchanged over the period 1975–1981 because the positive effects of California's strict emission control measures were balanced by the rapid population growth in this region.

For further exploration of this, Table I lists published ozone data for the CSCAB for the period 1975–1981. It is evident that 1979 was the peak year for ozone; subsequently the maximum O_3 value droped to 0.37 ppm in 1981 (below the value of 0.39 ppm in 1975). The increase in ozone levels from 1975 to 1979 and the significant decrease in 1980 and 1981 are also shown in other statistically valid quantities in Table I such as the numbers of first- and second-stage O_3 episodes during this 7-year period. Indeed, if we were to follow Innes' logic, one would have to conclude that while catalytic converters and other NO_x controls were ineffectual from 1975 to 1979, they became highly effective in reducing ozone levels in the Los Angeles basin in the period 1979–1981!

Table I. Selected Air Quality Data for California South Coast Air Basin[a]

	highest hourly av O_3 concn in basin, ppm	no. of first-stage O_3 episodes basin wide	no. of second-stage O_3 episodes basin wide
1975	0.39	119	8
1976	0.38	102	7
1977	0.39	121	11
1978	0.43	117	23
1979	0.45	120	17
1980	0.44	101	15
1981	0.37	100	5

[a] Taken from air quality data published by the CARB and the South Coast Air Quality Management District.

There are also problems with Innes' chemical mechanisms and his interpretation of smog chemistry. His OH + HCHO rate constant is a factor of ~4–5 too high (23) and, more important, NO_3 photolysis in daylight and the rapid back reaction of N_2O_5 to $NO_2 + NO_3$ (7, 8) were both ignored. The latter omission makes his eq 24–29 invalid. Moreover, the particular 6-h irradiations he refers to are not (as he claims) equivalent to 1-day solar irradiations. In fact they are only equivalent to about 50% of the total solar flux for a day near the summer solstice in the Los Angeles basin.

Another major concern is Innes' superficial and misleading treatment of the possible health and ecological effects of NO_2 and nitric acid. He states that in Los Angeles "the Federal NO_2 exceedance ($\approx$0.06 vs. 0.05 ppm) appears unimportant vs. the Federal ozone exceedance (0.40 vs. 0.12 ppm)." He then goes on to say "This is particularly true because of the trade-off involved in the reaction NO + O_3 → NO_2 + O_2, together with the 10/1 ratio for $(NO_2)/(O_3)$ for an equivalent health effect."

We find it remarkable that Innes compares annual averages for NO_2 (0.06 ppm vs. the AQS of 0.05 ppm) and then relates the result to the 1-h "Federal ozone exceedance". As a resident of California, he should be aware that the state for years has had a short-term AQS for NO_2 of 0.25 ppm hourly average. Surely for the sake of consistency in comparisons between ambient air quality data and AQS, this hourly average should have been used, together with the fact that during the period 1975–1980 in the Los Angeles basin the yearly highest hourly average NO_2 concentrations ranged from 0.41 to 0.61 ppm. Clearly some cities in the CSCAB do indeed have a significant nitrogen dioxide problem; this will intensify if NO_x emissions are increased.

As atmospheric chemists we do not feel qualified to comment in detail on the health trade-offs involved in the NO_x vs. O_3 controversy. However, while Innes raises the issue, he does not explore it adequately. Thus, we feel compelled to cite briefly both from his references as well as the findings of other workers. First, he cites a 10/1 ratio for "equivalent" $(NO_2)/(O_3)$ health effects from the report "Human Health Damages from Mobile Source Air Pollution: A Delphi Study" (24). In this study a variant of the Delphi technique was used to arrive at a consensus judgment of a group of medical experts on the nature of dose–response relationships for photochemical oxidants NO_2 and CO. Innes does not point out that in this report these experts concluded (24) "In contradistinction to the uniformity of opinion concerning the dose–response relationships for oxidant exposures, almost all of the estimates for nitrogen dioxide lacked significance. Group agreement

did not occur for any values among the normal adult, child or elderly population groups. This is not surprising since few human studies of the effect of acute exposure to nitrogen dioxide have been performed, and these have usually tested respiratory function rather than clinical response."

It has also been reported that the "World Health Organization Task Group on Environmental Health Criteria for Oxides of Nitrogen concurred on the 0.5 ppm adverse effects level and stated further that 0.1 to 0.17 ppm no more than once a month was consistent with protection of the public health" (25).

An additional health aspect of photochemical smog is that not just O_3 and NO_2 but also a spectrum of gaseous and particulate noncriteria pollutants are inhaled (9). These, though present in much lower concentrations, may have disproportionately large health impacts. The atmospheric levels of a number of these compounds are directly related to NO_x emissions. Nitrous acid is a key example and, as noted above, on Aug 8, 1980, we showed that its ambient concentrations near DTLA exceeded 6.5 ppb for the entire period 0200–0700, peaking at ~8 ppb at 0500 (12). At present the health effects of inhaled nitrous acid vapor are not known.

Also important is the fact that increased NO_x emissions may also lead to higher levels of a spectrum of nitroarenes present on combustion-generated particulates. Certain of these nitropolycyclic aromatic hydrocarbons are strong direct mutagens in the Ames *Salmonella typhimurium* reversion assay. One of them, 1-nitropyrene, not only is a major contributor to the strong mutagenicity of extracts of diesel particulates (26, 27) but also has recently been reported to be a strong animal carcinogen (27).

Finally, Innes' comments on the ecological impacts of nitric acid are so contrary to contemporary thinking and evidence [including very recent acid fog measurements in the CSCAB (19)] that they do not warrant discussion. Spicer's recent experimental data (17), on the other hand, are highly relevant to this issue. He states "There is an obvious linear relationship between the two variables, suggesting that strategies to control nitric acid formation must be based on NO_x emissions reduction. Limited reduction of organic emissions, a procedure used to control O_3, will have little affect on the ultimate nitric acid concentration. Strategies which allow NO_x emissions to increase as a means of inhibiting O_3 formation will be detrimental due to increased downwind concentrations of HNO_3."

In conclusion, on the basis of the best available scientific evidence, we remain convinced that continued strict control of both NO_x and HC is essential to protect both public health and the environment from a broad spectrum of impacts of photochemical smog; relaxation of NO_x controls would be a grave error.

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SIR: In response to the statements of Pitts et al. relative to my paper (*Environ. Sci. Technol.* **1981**, *15*, 904) I wish to make the following comments:

Background effects due to glass wall chamber surfaces appear to increase photooxidation rather than decrease it as evidenced in general by excess NO photooxidation with a clean chamber vs. gas-phase predictions. Chamber ozone

levels would be expected to be high rather than low. Such background effects in any case would not be expected to significantly alter relations between NO_x and ozone levels.

The effects of NO_x emissions on PAN are covered in our ref 17, where it was shown on the basis of Pitts' chamber work that PAN formation decreases with initial NO_x levels at HC/NO_x corresponding to Los Angeles emissions. More data showing this were recently reported by Glasson (American Chemical Society Meeting, April 1982).

Pitts et al. admit that adverse effects from the very low levels of nitric and nitrous acids in the atmosphere have not been demonstrated. The 8 h HNO_3 work place standard per the Government Industrial Hygienists is 2 ppm vs. a peak value of a few ppb in the atmosphere per Pitts et al., while nitrous acid is not listed as a toxic pollutant (1981–1982 Handbook of Chemistry and Physics"; CRC Press).

The biological effects of such acids (e.g., oxidation of cell wall lipids), whether present as gas or fog, depend on the buffering capacity of biological fluids, since they are strong oxidizing agents only at a low pH. Buffering capacity probably far exceeds inhaled acidity (~ 0.1 mg of HNO_3/day) from these components under worst conditions. The ammonia content of expired air is equivalent to 0.26–19 mg/day HNO_3 (Larson, T. V.; et al. *Science (Washington, D.C.)* 117, **1977**, 161) if breathing rate is taken as 10 m^3/day.

We are indebted to Pitts et al. for the update on ozone levels. The primary point I wished to make was that NO_x controls had offset the benefits of HC controls, and this conclusion still seems justified. Decreased driving because of higher fuel costs in this period also needs consideration in analyzing recent trends.

The rate constant used by us for the reaction HCHO + OH is higher than the reported literature value. Reasons for this are discussed in ref 7. The value is based on HCHO disappearance on irradiation and does not consider other HCHO reactions (e.g., HCHO photolysis).

As indicated in our article, treatment of reactions involving NO_2, O_3, OH, NO_3, and N_2O_5 was not intended to be rigorous. Not enough information on rate constants and concentrations for the various reactants are available for this. However, the assumptions made do appear to lead to a fairly good data fit.

The paper deals with metropolitan centers throughout the U.S. so that it is more appropriate to consider national than state air standards. The California 1-h standard of 0.25 ppm NO_2 was established 12 years ago on the basis of emphysema health risk inferred from studies on rats rather than any human effects. Later animal work showed emphysema effects only at much higher levels (~ 30 ppm). No formal review of the NO_2 air standard appears to have been made even though extensive work has failed to show significant human health effects below 1–2 ppm. The 10/1 ratio (NO_2/O_3) for equivalent health effects still seems valid based on much additional information. Industrial hygienists still have an 8-h work-place standard of 5 ppm for NO_2 vs. a 0.1 ppm standard for O_3. Harmful effects that have been found at high NO_2 levels (oxidation of cell wall lipids) would not be expected at lower levels even on a proportional basis because of the extreme effect of pH on nitrate or nitrite oxidation potential (see above).

With respect to multiday episodes, nighttime effects, etc., negating the conclusions that NO_x controls are counterproductive, it is pertinent that Pitts' studies substantially took this into account by using a surrogate organic composition that included a major formaldehyde fraction. Limited tracer studies do not appear to show that leftover products are a major organic component, while

initial ozone level is near zero for all days.

Although total radiation involve in Pitts 6-h runs is about half the theoretical maximum for the summer solstice, several factors combine to make the effective average irradiation during the summer–fall smog season much less. These include the following: downwind emissions, which are exposed to less radiation than initial components; radiation absorption by smog, fog, and clouds; increased zenith angle after the summer solstice. The studies of Jeffries et al. and Stephens et al. analyzed in our ref 7 show that 6 h of irradiation under Pitts et al. chamber conditions has about the same effect on NO oxidation as the radiation from one typical "sunny" summer–fall day.

In regard to ecological impacts of nitrates, it now seems very clear from several papers presented at the recent Las Vegas Spring American Chemical Society Meeting that such compounds have no long-term adverse effect on lake pH because they are rapidly assimilated by vegetation (ACS Division of Environmental Chemistry; Abstr 22, 500, 530; American Chemical Society: Washington, D.C., 1982). Rather nitrates are beneficial because they act as important plant nutrients. This view is further supported by McLean (*JAPCA*, **1981**, *31*, 1184–1187). Sierra lakes show essentially no change from near neutral pH in the last 16 years (*Calif. Agric.*, **1981** May–June).

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SIR: Since we also are concerned about the environmental air quality and health in the Los Angeles (LA) Basin if a less than optimum pollution control strategy were pursued, we feel obligated to reply to the preceding comments of Pitts et al. (*1*) concerning our earlier article (*2*). The major conclusion we reported was simply this: a reduction of the vehicular NO_x emission standard (from 1.0 to 0.4 g/mi) for the purpose of controlling ozone (O_3) in the LA Basin would be counterproductive because it would likely lead to higher ozone both in LA and along the entire downwind corridor to San Bernardino. We feel that this central conclusion and the scientific evidence supporting it stand unshaken. In their comments, Pitts et al. (*1*) cite three separate articles. This reply, however, will be restricted to those comments pertinent to our work, which was independent of that reported by Glasson (*3*) and by Innes (*4*).

Pitts et al. (*1*) never challenge our basic conclusions. Instead, they raise the following issues: (1) adequacy of the ELSTAR model; (2) the interpretation of modeling and smog chamber results, in general; (3) acid precipitation; (4) health effects of pollutants. We shall address the first two issues in detail, and we shall comment on the last two issues, though these two issues are beyond our present fields of expertise (as well as those of Pitts et al. (*1*)).

(1) The Adequacy of the ELSTAR Model. Pitts et al. (*1*) contend that we have applied a model of limited reliability to the California South Coast Air Basin (CSCAB). However, the procedure followed in developing the ELSTAR model gives us confidence that this model is applicable to and reliable for the CSCAB. Lloyd et al. (*5*) first developed and tested the ELSTAR chemical mechanism alone with smog chamber data from the

University of California at Riverside. They then used ambient CO data collected in the CSCAB during the Los Angeles Reactive Pollutant Program (LARPP) to refine and test the meteorological submodel. Finally, predictions of the complete model (emissions, meteorological, and chemical submodels) were compared against the O_3, NO, and NO_2 ambient measurements taken during LARPP.

LARPP was specifically designed for testing Lagrangian or trajectory models such as ELSTAR. Zak (6) has reviewed LARPP and Calvert (7, 8) and Angell et al. (9, 10) have analyzed sections of the data. During a LARPP day, a parcel of air, marked by tetroons, was followed through the LA Basin. Measurements of the concentrations of different chemical species in the air parcel were made by helicopter from 60 to 250 m and occasionally to 400 m. These measurements plus the measurements at the surface stations provide a data base for the LA Basin with unusually good vertical resolution. Generally, model results can be compared only against surface measurements (11, 12). For ELSTAR, however, model results were compared against the combined surface and elevated measurements of LARPP, which is a more stringent test of the model than a comparison against surface measurements alone. Thus, ELSTAR has been validated against ambient data for the CSCAB so that in our application of this model we are not simply extrapolating smog chamber data to the atmosphere.

Pitts et al. (1) criticize the chemical mechanism employed in ELSTAR "as being outdated and deficient in several respects", but they do not offer any specific arguments or evidence to support their claim. Recently, we (13) compared the ELSTAR mechanism with the EPA (14, 15), the Falls, Seinfeld, and McRae (12, 16), and the carbon bond II (17, 18) mechanisms for standard and city-specific EKMA conditions (19, 20). Under these conditions all four mechanisms showed inhibition of O_3 formation by NO_x, but the other mechanisms actually showed *more* inhibition than the ELSTAR mechanism. This suggests that the results reported in our earlier article (2) would be qualitatively the same had we employed the EPA, the Falls, Seinfeld, and McRae, or the carbon bond II mechanism, rather than the ELSTAR mechanism, in our trajectory simulations.

Pitts et al. (1) criticize our simulation of only single-day events, which they claim ignores the impact of day-to-day carryover of pollutants. Actually, the effect of day-to-day carryover is incorporated in the initial conditions in the daytime simulation. Therefore, if reliable initial conditions for the reactants are available, there is no reason to require a model to first demonstrate its ability on multiday simulations before being considered acceptable. Since there are no regular upper-level measurements of major pollutants (let alone other trace species) anywhere at any time of the day, the determination of the initial conditions in a daytime simulation is, in fact, quite difficult. Indeed, a multiday model simulation is an attempt to reduce the impact of uncertainties in the initial conditions (of the first day) on the pollutant concentrations of the second and subsequent days. However, a multiday simulation has problems of its own. In particular, knowledge of nighttime pollution chemistry is minimal; it is not clear whether switching off the photochemistry is sufficient to describe the nighttime reactions since reactions that can be ignored during the day may become dominant at night. Secondly, it is not yet clear how extensively numerical errors accumulate in a multiday simulation. We are aware of and concerned about the initial-condition problem. This is why we chose Oct 15, 1973, as one of the days in our study since, on that day, elevated measurements of many chemical

species were available as part of the LARPP study. These measurements provided us with guidelines in specifying realistic initial conditions.

Pitts et al. (1) emphasize that the early morning concentrations of HCHO, higher aldehydes, HONO, and peroxyacetyl nitrate (PAN) are important in determining the results of atmospheric simulations. In our paper, we describe our procedure for estimating the initial concentrations of HCHO and higher aldehydes and list the initial concentrations used for these species in the base-case simulations. The initial concentrations of HONO and PAN are not supplied by the user of ELSTAR. Instead, ELSTAR computes the initial concentrations of HONO and PAN at each vertical elevation from steady-state relations involving the initial concentrations of other species (5). For our base-case simulations, the initial HONO concentration at ground level was 0.2 ppb for trajectory 073115 and 1.7 ppb for trajectory 101517, and the initial concentrations decreased with increasing elevation. Recently, Harris et al. (21) measured maximum predawn HONO concentrations ranging from 0.4 to 8.0 ppb in the LA Basin. Both Harris et al. (21) and Platt et al. (22) found that the HONO concentration declined very rapidly after sunrise to levels below their detection limit (about 0.2 ppb). Since our trajectory 073115 began 105 min after sunrise and trajectory 101517 began 50 min after sunrise, the initial HONO concentrations used in our simulations are consistent with the measurements of Harris et al. (21) and Platt et al. (22). The initial PAN concentrations obtained by ELSTAR from the steady-state relations are quite low, less than 0.4 ppb for the base cases. However, these concentrations are consistent with the measurements of Tuazon et al. (23). On Oct 13, 1978, a day on which the peak O_3 was 454 ppb, Tuazon et al. (23) found the PAN concentration to be below their detection limit (3 ppb) from 0430 to 0700 PST.

Pitts et al. (1) further state that stratification of pollutants under stable conditions cannot be simulated by models validated against smog chamber data. In actual fact, only the chemical submodel of an airshed model is validated against smog chamber data, and it is the meteorological submodel, not the chemical submodel, that is responsible for describing pollutant dispersion, including stratification.

Pitts et al. (1) point out many discrepancies between the model's base-case predictions and the "actual" air quality data. As described fully in our paper (2), ambient data from one to three nearby monitoring sites were interpolated, both in space and in time, to produce rough pollutant estimates at the hourly locations along the trajectories. The quality of the estimates actually deteriorates for primary pollutants such as CO and NO, which are sensitive to local sources. One should also realize that measurement errors add further uncertainties to the interpolated pollutant concentrations. For ozone, calibration errors alone for instruments used in the early 1970s were about 15% (12).

Pitts et al. (1) claim to have found significant discrepancies between the interpolated values and model predictions even for primary pollutants and go on to conclude that one cannot have "a great deal of confidence" in the model predictions for the secondary pollutants. Unfortunately, while they profess to give the reader some perspective on what constitutes good and acceptable agreement, they clearly show bias by choosing examples that indicate only underpredictions by the model. They compare the predicted and interpolated values for specific hours, but one should also look at the range of concentrations involved. For example, both the predicted and

pollutant	model	data base[a]	corr coeff	mean of residuals, ppm	std dev[b] about the mean of residuals, ppm
O_3	ELSTAR	6 LARPP days	0.84	0.0172	0.0197
	Caltech	6/26-27/74	0.89	-0.0019	0.0382
	SAI	6/26/74	NA[d]	0.03364	0.04414
		6/27/74	NA	0.00898	0.04192
NO_2	ELSTAR	7 LARPP days	0.49	0.0270	0.0387
	Caltech	6/26-27/74	0.67	-0.0078	0.0348
	SAI	6/26/74	NA	-0.02414	0.02976
		6/27/74	NA	-0.02550	0.03427
NO^c	ELSTAR	7 LARPP days	0.62	0.0223	0.0350
CO^c	ELSTAR	6 LARPP days	0.55	0.20	0.95

[a] The data selected for calculating the statistics vary from model to model, and this may affect comparisons between models. For example, inclusion of nighttime data tends to improve the performance statistics of a model. The statistics for the ELSTAR model use only daytime data. The statistics for the Caltech model use both daytime and nighttime data. The O_3 statistics for the SAI model use only periods with observed O_3 concentrations greater than or equal to 0.08 ppm. [b] For the ELSTAR model, standard deviation about the mean of residuals is unavailable; instead, the mean of absolute residuals is given. [c] No comparable statistics are available for the Caltech and the SAI models. [d] Not available.

interpolated concentrations of CO and NO remained relatively low and flat for trajectory 073115 (Oct 31, 1973). Clearly, a factor of 2 difference in the low concentration region (which is not at all uncommon for a current airshed model) is not as serious as in the high concentration region. That is why we consider the CO predictions acceptable. In the case of NO, the shapes of the predicted and interpolated curves are similar. This additional property led us to conclude that the NO predictions for trajectory 073115 were good.

The performance statistics of current models have been described by their developers. Thus, ELSTAR was compared against the LARPP data; the Caltech (24) and SAI (25) models were compared against the ground-level measurements of June 26 and 27, 1974. Some of these statistics are presented in Table I. The quoted statistics are insufficient to characterize completely the performance of a model, but we do see that these models have comparable performance statistics. Therefore, the contention of Pitts et al. (1) that the ELSTAR model is poorer than the state-of-the-art airshed models is unfounded.

(2) The Interpretation of Modeling and Smog Chamber Results. Pitts et al. (1) are concerned that we arrived at our conclusions on the basis of results of only a few hypothetical trajectories. However, the trajectories are realistic, and they are typical of the flow pattern in the CSCAB. More important, our results are a manifestation of the well-known NO_x-inhibition effect. The O_3 reduction by NO_x inhibition occurs all along the trajectories because of the continuous exposure of air parcels to fresh NO_x emissions.

The inhibitory effect of NO_x emissions on O_3 levels in the CSCAB has also been confirmed in other studies. In a study done by Systems Applications, Inc. (26), for the California Air Resources Board, O_3 concentrations were modeled for a typical high-O_3 day at five selected stations in the CSCAB. These five stations often experience high O_3 concentrations and the average modeled concentration on this day in 1974 was 0.34 ppm. With a 50% uniform reduction in non-methane hydrocarbon (HC) emissions, the average predicted concentration dropped to 0.25 ppm. However, when NO_x emissions were reduced by 25% in conjunction with the 50% HC reductions, the average O_3 levels increased from 0.25 to 0.27 ppm. With a 50% reduction in NO_x emissions (accompanied by a 50% HC reduction), the O_3 levels were 0.27 ppm, still above the levels achieved with just the HC emission reductions. Similar results were observed when NO_x emissions were reduced in conjunction with a 75% reduction in HC emissions.

In a scenario study using a trajectory from downtown LA to Pasadena on June 27, 1974, Seinfeld and McRae (27) investigated the impact of vehicle NO_x control on the peak O_3 concentration along the trajectory for the year 1987. With the HC emission level for the SCAB held fixed at 680 tons/day in 1987 and with standard deterioration factors for vehicle emissions included, a 1 g/mi NO_x standard by 1982 would give a total NO_x emission level of 1153 tons/day and a peak O_3 of 0.30 ppm. Changing the NO_x standard to 0.4 g/mi would change the total NO_x emissions slightly, to 1137 tons/day, with no change in peak O_3 values, but a 0.4 g/mi NO_x standard with no deterioration would give a total NO_x emission of 1063 tons/day and an increase in peak O_3 concentration to 0.31 ppm.

In a more recent work, Costanza and Seinfeld (28) studied optimal emission control strategies to reduce ambient O_3 air quality standard violations in the LA Basin. Optimality was defined as minimizing a total cost function consisting of control cost and a cost associated with O_3. They made use of a diagram relating the precursor emissions to the number of days with O_3 exceeding 0.10 ppm and the estimated emission control costs, both developed by Trijonis (29). They examined the paths suitable for reducing only O_3 violations. Based on a calculus of variations technique, it was found that the optimal emission control path, in terms of control costs, calls for reductions in HC emissions alone and no net change in total NO_x emissions. In another study, Stephens (30) concluded that control of HC is the best way to achieve O_3 reduction. He further stated that since control of NO could actually impede progress toward O_3 control and since O_3 appears to be the more serious (of O_3 and NO_2) health hazard, HC control should take precedence over NO control.

The Environmental Protection Agency has recommended (31) the use of their Empirical Kinetic Modeling Approach (EKMA) for determining HC control requirements necessary to achieve the ambient O_3 air quality standard. In the EKMA approach, O_3 isopleths are generated as a function of initial HC and NO_x concentrations. The slope of the O_3 isopleths in the region of low HC/NO_x ratios is a measure of the NO_x inhibition effect; the greater the slope of the isopleths relative to the NO_x axis, the greater the inhibition effect. The standard EKMA O_3 isopleths indicate a NO_x inhibition effect for HC/NO_x ratios less than about 8.

In a number of recent papers (21, 32, 33), Pitts and co-workers have generated EKMA-type O_3 isopleths by using their Statewide Air Pollution Research Center propene/n-butane/formaldehyde mechanism. They have generated O_3 isopleths by assuming a continuous NO_2-dependent radical source (32), various initial concentrations of HONO (21), and different representations of the HC mixture (33). It is noteworthy that in each of these cases, O_3 isopleths indicate a substantial NO_x inhibition effect (even more than that present in standard EKMA isopleths) for HC/NO_x ratios as high as 15.

Although Pitts et al. (1) have strong reservations about applying smog chamber results to the atmosphere, their concern apparently does not extend to the smog chamber results of Spicer (34). They quote his smog chamber results at length and indulge in unwarranted extrapolation of those results to ambient levels in the LA Basin. Their quotation from Spicer that 25–50% of initial NO_x can be converted to organic and inorganic nitrate within the first three hours of reaction is made without Spicer's qualifying remarks. For example, Pitts et al. (1) fail to mention that in these experiments the starting NO_2/NO_x ratio was 0.5, which is not typical of morning ambient conditions. A few hours of photochemistry is generally required to achieve that ratio. In urban air, continuous injection of HC and NO_x emissions, which was not simulated in Spicer's experiments, would also influence the ambient NO_2/NO_x ratio. Furthermore, conversion of 25–50% of initial NO_x in 3 h, as quoted by Pitts et al. (1), amounts to an average characteristic conversion time of 6.4 h and a 16% h^{-1} conversion rate. This conversion rate seems too high for ambient conditions. For example, Calvert (35) estimated the NO_x conversion rate to be 8% h^{-1} for data collected in the LARPP study. Finally, in interpreting Spicer's chamber results, Pitts et al. (1) note a "good nitrogen balance" in those experiments and infer that the application of the results to ambient conditions will not be clouded by imperfectly understood chamber wall effects. However, it should be pointed out that this nitrogen balance was obtained by assuming a rather high wall loss rate of HNO_3 of 64% h^{-1} (1.07×10^{-2} min^{-1}).

(3) Acid Precipitation. On several occasions, Pitts et al. (1) raise the issue of acid rain and acid fog. In each instance, no specifics are provided. It is not surprising that in the LA Basin, where HNO_3 levels of 10–30 ppb (15) have been observed, fogs can occasionally have rather low pH values. For example, an initial HNO_3 concentration of 15 ppb and a fog water content of 1 g/m^3 can result in a pH as low as 3.2. However, as the fog burns off, all the HNO_3 will be transferred back to the gaseous phase barring any reactions with basic materials like ammonia and soil dust. The effects of such short-lived acidic fogs, if any, are not known at this time. While the role of nitric acid in the effects of acid precipitation is not yet definitive, existing information (36–38) indicates that nitrate would not lead to soil or lake acidification as it would be rapidly metabolized in most ecosystems. This is because when NO_3^- is biologically utilized in the watershed, there is an associated release of basic anions such as HCO_3^- or OH^-.

(4) Health Effects of Pollutants. Pitts et al. (1) state that, as atmospheric chemists, they are not qualified to comment in detail on the health-effects trade-off in the NO_x vs. O_3 controversy. Neither are we. However, since they raise the issue and criticize our lack of comment, we feel compelled to point out (from their source (39)) that while human health effects from O_3 levels of 0.5 ppm have been documented, it is the absence of adverse effects from NO_2 levels up to 0.5 ppm that has also been noted. Indeed, if they had quoted Sterns (39) accurately on the 1977

World Health Organization (WHO) position (40) or cited studies on NO_2 health effects from their own Statewide Air Pollution Research Center (41–43), we could see that the NO_2 levels at 0.5 ppm do not show adverse human health effects. For that reason the WHO considered a short-term NO_2 standard of 0.10–0.17 ppm to be quite protective (40, 43). In fact, in discussing the human health effects of NO_2, a recent National Academy of Sciences study (44) on vehicular NO_x emissions reports: "A substantial series of studies fails to show any clear-cut evidence for effects on pulmonary function at exposures of 1 ppm or below." Note that NO_2 levels of 1 ppm are not reached in the LA Basin; even 0.5 ppm is attained as a 1-h average only once or twice per year. On the other hand, O_3, which is 5–10 times more toxic than NO_2 at the same concentration (41), reaches 0.3 ppm in the LA Basin several times each year. Therefore, one cannot help but agree with California medical authorities that O_3 formation "is the single most important health-related consequence of NO_x emissions in the Basin" (41). Neither of the O_3 control strategies discussed in our article would result in NO_2, HNO_3, or PAN levels as high as those produced under the pre-1980 vehicular emission standards; furthermore, the less stringent NO_x standard should result in lower O_3 levels in most areas of the CSCAB.

Pitts et al. (1) go on to speculate that other nitrogen-bearing compounds may be formed as a result of NO_x emissions and that they may (or may not) ultimately prove to be health hazards. Our simulations (2) did not focus on these compounds, none of which (as they acknowledge) are known to have any human health effects. We simply point out that the unsupported speculations by Pitts et al. (1) have been explored elsewhere in the literature (45–49) and do not constitute adequate evidence for stringent NO_x controls.

To summarize, we have addressed the comments of Pitts et al. (1) on the technical aspects of our simulation study and have shown these comments to be unjustified. Their remaining comments are, in essence, merely speculations on the hypothetical adverse effects of trace nitrogenous compounds through which they imply that NO_x emissions should be reduced to the maximum extent possible. In so doing, they ignore the implications of this strategy for O_3, a pollutant with recognized health effects at levels attained in the LA Basin. We believe that the environmental quality and public health of the LA Basin will suffer if, in controlling emissions, the overwhelming scientific evidence for NO_x inhibition is ignored. Our simulations (2) and those of others (21, 26, 27, 28, 30, 32, 33) all show that ambient O_3 concentrations are not directly proportional to NO_x emissions and, indeed, that NO_x emissions can inhibit O_3 formation. We point out further that both of the NO_x emission scenarios considered in our simulations assumed vehicular NO_x emission standards below the pre-1980 standards. Our finding that the more effective approach to reducing O_3 corresponds to the less stringent NO_x emission scenario stands unaltered.

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SIR: This note was generated as a reply to the correspondence submitted by Pitts et al. in which these authors comment on various papers, including "Effect of Hydrocarbon and NO_x on Photochemical Smog Formation under Simulated Transport Conditions" (Glasson, W. A. *J. Air Pollut. Control Assoc.* **1981**, *31*, 1169).

Pitts et al. have criticized my work on O_3 formation with the intent of weakening our arguments against NO_x control by citing evidence on nitric acid and particulate nitrate formation which they interpret as supporting stringent NO_x control. The present note comprises a rebuttal to that criticism and suggests a more objective approach to analyze evidence for or against NO_x control measures.

Although in the words of the oft-used cliche there is room for honest men to disagree, the authors are attempting to impose their own interpretations on the reader as opposed to those of the primary authors. A case in point is the quotation from my paper (1) regarding the negation of the effects of HC control on O_3 by imposition of NO_x control. A more balanced quotation would have been my conclusion: "Thus, hydrocarbon control will reduce O_3 consistently and result in a modest NO_2 reduction while NO_x will increase O_3 in the urban areas and have little effect elsewhere, but will reduce NO_2 consistently. The trade-off involved with NO_x control should be considered in public policy decisions." The point is then that decisions must be reached on NO_x control in light of the contrasting effects of NO_x on O_3 and NO_2.

Further, the authors make certain unfair criticisms of my experiments such as "data [were used] from experiments carried out in smog chambers under highly restricted and artificial conditions (e.g., irradiations at constant light intensity of 6–22-h duration) and readily extrapolate them to the ambient atmosphere." With regard to the effect of light intensity, the use of a constant light intensity for an irradiation time chosen to achieve a total integrated light intensity comparable to that of Los Angeles is an approximation, clearly, but work has been reported indicating that it is a reasonable assumption. I quote from the paper by Darnall et al. (2): "The data reported here show that irradiations carried out at constant light intensities will result in virtually the same O_3 yields at 5–6 and 10–12 hours as irradiations carried out with a diurnally varying light intensity with the same total radiation dosage." This result was also obtained by Jaffe (3) and in our laboratory (4). Our diurnal light intensity experiments (4) also showed the same effect of HC and NO_x as constant intensity experiments. Further, my work has been criticized by Pitts et al. for readily extrapolating our results to the ambient atmosphere. On the contrary, a short section was included in ny paper discussing the shortcomings of the experimental model for simulating chemistry in the ambient atmosphere.

Although I agree that carryover effects can influence the photochemical processes occurring in smog formation, the results of Harris et al. (5) from a computer modeling study of the effect of early morning HONO indicate that only small increases in O_3 would be expected and that the peak O_3 occurs at about the same irradiation time. Such perturbations should not affect the overall conclusions of my paper.

The concept of unknown radical sources that are necessary to obtain computer modeling fits of experimental data is consistent with the dirty chamber effects reported several years ago (6). Such effects are undoubtedly chamber-specific phenomena. A recent study by Sakamaki et al. (7) modeled the C_6H_6–NO_x system and did not require the use of an unknown radical source to achieve a reasonable fit. It is probably significant that the chamber used in the Sakamaki et al. study can be cleaned thoroughly between experiments. The effect of such extraneous radical sources on the dependence of O_3 formation on HC and NO_x concentrations is still open to question.

With regard to the authors' comment that no PAN or HNO_3 data were reported in my paper, this is clearly correct. However, the results from this laboratory of the study done with diurnal light intensity (4) variation include data for PAN. It was found that the effects on PAN closely parallel the effects of HC and NO_x on O_3 formation, i.e., HC reduction reduces PAN at all NO_x levels studied while NO_x reduction can increase or have little effect on PAN depending on the HC concentration.

The authors cite the work of Spicer et al. (8) and state that "for a given HC mix, there was a linear relationship between $(HNO_3)_{max}$ and initial NO_x concentrations." This is only partially true, since Spicer's data show a linear dependence of $(HNO_3)_{max}$ on $(NO_x)_0$ up to 0.45 ppm NO_x (4.5 ppmC NMHC) and up to 0.3 ppm NO_x (1.5 ppmC NMHC). The authors further quote Spicer: "At HC/NO_x ratios typical of morning conditions in many cities, i.e., about 5–10, 25–50% of the initial NO_x can be converted to org. and inorg. nitrate within the first 3 h of reaction." The next sentence in Spicer's paper reads "The chamber experiments started with a NO_2/NO_x ratio of 0.5, which would typically require about 2 h of reaction to achieve in urban air, so these Fn values (fractional conversion of NO_x to products) are probably more representative of urban air after about 5 h of irradiation." Thus, conversion of NO_x to products occurs more downwind of the urban area than represented by the authors, and dilution of the transported air mass becomes more significant.

The authors' statement that "increasing NO_x emissions will ultimately lead to a proportionate increase in nitrate levels" is an oversimplification of the situation since Spicer's data (8) show a less than linear dependence of $[(HNO_3)_{max} + (PAN)_{max}]$ on the initial NO_x concentration at NO_x and HC concentrations of atmospheric interest (0.1–0.6 ppm NO_x and 1.5 annd 4.5 ppmC NMHC).

I generally agree that the *ultimate* fate of NO_x in the atmosphere is nitric acid and/or particulate nitrate. However, it is important to consider how fast NO_x is converted to these species and, therefore, what segment of the population is being exposed to them. It has been demonstrated in my work (1) that effective control of O_3 formation can be achieved through HC reduction but that NO_x reduction may be counterproductive for O_3 control. In addition NO_x reduction may not decrease and could possibly increase population exposure to nitric acid and nitrates. It would be appropriate to test the effects of various control strategies by using available atmospheric models in order to arrive at an optimal control strategy. Thus my original conclusion: "The trade-off involved with NO_x control should be considered in public policy decisions" is still pertinent to this important issue.

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Comment on "Approach to Forecasting Daily Maximum Ozone Levels in St. Louis"

SIR: The article by Prior et al. (1) which appeared in the April 1981 issue of *Environmental Science and Technology* makes some significant technical contributions that merit discussion.

The authors' statement that "a test of the effectiveness of . . . [a] . . . forecasting model is to examine the ability of the model to predict ozone episodes" is true. They should have been more emphatic—it is *the* test of any ozone model. The fact that they clearly recognize "ozone episodes" as being distinct and important events and endeavor to deal with them is in itself a significant contribution. In too many cases there has been a tendency to relegate episodic days to the realm of "outliers" and simply ignore them. Yet from both theoretical and legal standpoints they are *the ballgame.*

I also believe that the authors' finding that the best regression variable for predicting daily maximum ozone is the ozone concentration at 9:00 A.M. is important. I have approached the same problem by looking for a correlation between maximum daily downwind plume ozone with maximum daily upwind ozone or "side" ozone (i.e., adjacent rural maxima) with some success.

It is my thesis that the atmospheric photochemical process is limited by the supply of free radicals with sufficient energy to attack hydrocarbons and sustain a chain oxidation process. Ozone via several mechanisms can yield such radicals. Therefore, the supply of input ozone can control the level of photochemical activity and the maximum concentration of secondary ozone that develops downwind. Input ozone either can be of stratospheric origin or can be transported from elsewhere. This thesis in no way exonerates anthropogenic pollutants as also being essential for the generation of high levels of downwind plume ozone.

This view does, however, change one's perception of the factors that limit the ozone on any given day. The almost total failure of episodic ozone maxima to correlate with either hydrocarbon or NO_x precursor concentrations in numerous studies simply points out that some other variable controls. It also explains the near total failure of hydrocarbons abatement to reduce ozone. If hydrocarbons are 10-fold in excess, reducing the excess to 5-fold will have little or no effect. This is particularly true if the real limitation on the process is free-radical population as controlled by input ozone. The finding of Prior et al. that 9:00 A.M. ozone is the best independent predictive variable is certainly consistent with this thesis. Ozone at 9:00 A.M. is a measure of "input ozone".

I do take issue with these authors when they suggest that a St. Louis episode might be attributed to the passage of incoming air over "the massive emission sources of the Ohio Valley". While there is probably validity in claiming the Ohio Valley to possess massive emission sources of TSP or SO_2, the claim is far less supportable for NO_x or hydrocarbons.

Blaming ozone episodes on transport has been popular recently. Thus Minnesota partisans blame a 140 ppb level observed in 1980 on Chicago, and authors speaking for the Northeast blame everything West—even Texas; and now Prior et al. in analyzing St. Louis point the finger at the Ohio Valley. Of course these views are politically popular but to date are supported by little scientifically solid evidence.

Few authors appear to have a true perspective of the vastness of the continental atmosphere when compared to that of the urban areas or of the potential of the atmospheric cleansing and dilution processes.

Anthropogenic hydrocarbons and NO_x simply cannot be transported for several hundred miles over one or more days elapsed time and arrive at concentrations capable of generating ozone levels significantly above the current standard such as found in and downwind of urban areas.

Neither can ozone at such concentrations be transported for such distances in the surface boundary layer. Dilution and destruction serve to substantially obliterate ozone plumes within 100 miles or less. Thus, except for urban areas in close proximity, one must accept the fact that high levels of photochemical ozone are derived from local pollutants.

In pollution-free atmospheres well above the surface of the earth, ozone itself is long lived. Thus ozone can at times survive along distance transport—but not at major concentrations. There is no way atmospheric dilution processes can be avoided.

Such transported ozone, while insignificant in concentration when compared to that found during episodes in downwind urban plumes, can be significant when compared to minimum ozone background levels. Thus transported ozone could increase a background of 50 ppb to perhaps 80 or even 100 ppb. This ozone in turn would increase background free-radical concentrations and the intensity of the photochemical smog process in polluted areas. Thus claimed instances of ozone transport may in reality be initiation phenomena.

The thesis that the influx of stratospheric ozone initiates surface photochemistry via free-radical processes has received more attention and rests on more substantial evidence. It is probable that widespread ozone episodes are the consequence of the widespread influx of stratospheric ozone behind cold fronts and in the back side of high-pressure air masses, not merely due to the direct transport of ozone.

Registry No. O_3, 10028-15-6.

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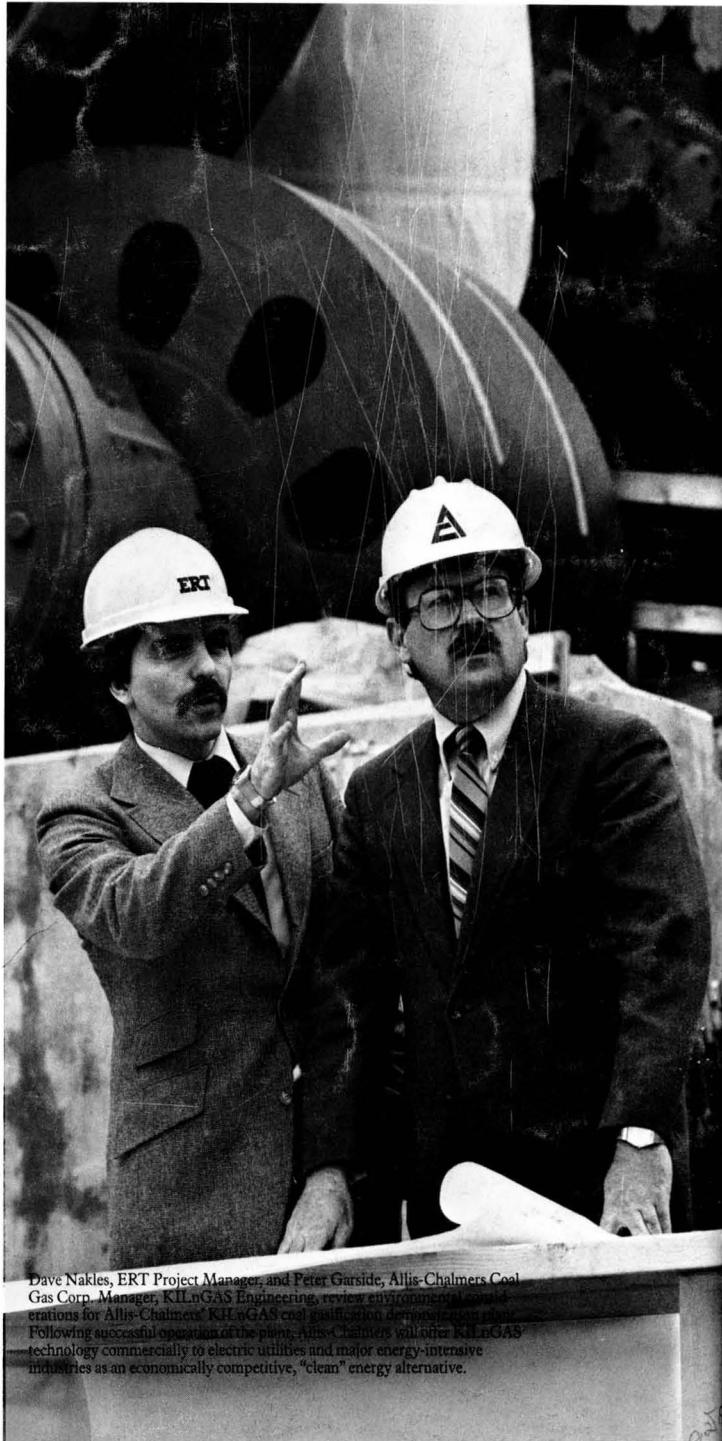
Dave Nakles, ERT Project Manager, and Peter Garside, Allis-Chalmers Coal Gas Corp. Manager, KILnGAS Engineering, review environmental considerations for Allis-Chalmers' KILnGAS coal gasification demonstration plant. Following successful operation of the plant, Allis-Chalmers will offer KILnGAS technology commercially to electric utilities and major energy-intensive industries as an economically competitive, "clean" energy alternative.